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TECHNICAL REPORT ECOM-01614-2

DEVELOPMENT OF THE HIGH RATE METAL-AIR DEPOLARIZED BATTERY

QUARTERLY REPORT No. 2

By

ALLEN CHARKEY

JUNE 1966

FOR

U. S. ARMY ELECTRONICS COMMAND

FORT MONMOUTH, N. J.

Prepared Under Contract No. DA-28-[illegible](E)

Project No. 1CO 14501 A-34A

By

YARDNEY ELECTRIC CORPORATION
New York, N. Y.

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UNITED STATES ARMY ELECTRONICS COMMAND · FORT MONMOUTH, N.J.

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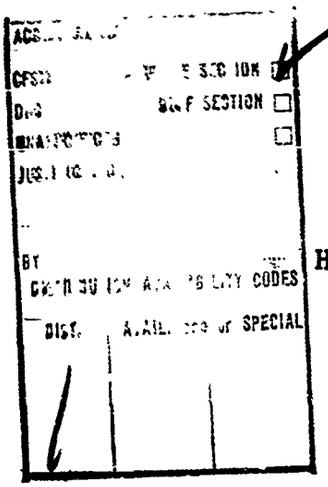

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4. ABSTRACT

This report covers the work done during the second quarter of the investigation for the U. S. Army Electronics Command. The study is being conducted to determine the performance characteristics and operational parameters for various metal-air couples. The anode materials being examined are Al, Ba, Ca, Mg, and Zn. They must discharge efficiently at any temperature from -25°F to 125°F at rates from the 30 minute to 50 hour.

The most favorable system in watt-hour per pound performance appears to be the zinc-air cell. During this quarter favorable high temperature discharge performance was obtained by keeping air spacing to a minimum.

Some of the problem areas encountered have been loss of water and excessive carbonation of the electrolyte at 120°F. This results in poor performance and decrease in shelf life.

Several methods for increasing activated shelf life at room temperature have been studied. The most promising appears to be the use of a "parasitic" drain across the cell terminals to delay flooding. At present, shelf life up to one month has been achieved with minimal capacity loss.

The investigation of the magnesium anode during this quarter has included a study of several electrolytes to determine compatibility with both electrodes. In all cases, best performance was obtained in a "free" electrolyte system.

The magnesium-air test cells, used only for exploratory studies, delivered specific energies of 50-55 Watt-hrs./lb. This could be improved substantially by increasing the thickness of the anode and decreasing the quantity of free electrolyte.

The investigation of calcium, aluminum, and barium air systems is still in an early exploratory stage. Particular interest however, is being given to calcium in an organic-aqueous electrolyte with various corrosion inhibiting agents. It appears that the air electrode will also function in this modified aqueous system.

Preliminary data for pure aluminum anodes is only moderately favorable in KOH electrolytes containing ZnO. The use of alloys to decrease corrosion appears warranted.

Heat transfer by means of air convection has been studied over the entire temperature range (-25 to +120°F) for the 2C through the C/50 rate of discharge. The testing units employed the zinc-air couple, but the heat transfer and air convection data are suitable for any metal-air battery design. This experimental investigation also indicated that low temperature bootstrap heating operation will be feasible for a zinc-air battery.

5. Body of Report

5.1 Air Electrodes

Several newly developed air electrodes were obtained for testing during the second quarter of work. These were several Pt types of activated electrodes made by Chem-Cell Corp. and American Cyanamid Co., along with a Ag/Hg catalyzed air electrode also made by American Cyanamid. The American Cyanamid electrodes tested were basically the AB-4X Pt type electrodes with a porous Teflon wetting-control membrane pressed onto the active surface.

Polarization characteristics for these electrodes were first determined at room temperature in both KOH and $Mg(ClO_4)_2$ electrolytes. The performance of the cathodes in these electrolytes were determined with the appropriate anodes, which were zinc and magnesium respectively.

Work in the first quarter demonstrated that the American Cyanamid air electrode, coded AB-4X and fabricated without flooding protection, delivered about one half of the capacity achieved with a zinc-air couple using the YEC "FP" air electrode. Use of a cellulosic wetting control membrane at room temperature inhibited the flooding. The new American Cyanamid Pt electrodes provided protection against flooding. It can be seen from Figure 1 that these electrodes (coded LBB-1, LAB-4X, LAB-4), deliver a full discharge with a minimum degradation in voltage due to flooding.

The American Cyanamid Ag/Hg electrode did not feature a wetting control membrane, and initial experimental work showed that this electrode exhibited higher polarization at room temperature than did the FSC cathode. Microscopic examination of the Ag/Hg electrode showed an unusually thick layer of catalyst. Although this would lengthen its life with respect to flooding and probably recrystalization effects, it impedes, however, the diffusion of oxygen through the cathode to the catalyzing surface. The rate of diffusion of oxygen to the electrolyte-cathode interface is reduced considerably at higher current densities. (See Figure 2). It can be seen that the American Cyanamid silver electrode, coupled with zinc, exhibited a cell voltage of 0.9 V. at a current density of .5 A/in^2, as compared with the FSC electrode which gave a current density of 1 A/in^2 at the same voltage.

Performance data for the newer American Cyanamid cathodes have also been obtained at low temperature. Figure 3 shows that the discharge characteristics at -30°C are similar to the AB-4X platinum electrodes. The air electrode polarized at a constant rate from the beginning of the discharge and no plateau potential was evident.

The platinum catalyzed air electrodes made by Chem-Cell Corp. were constructed differently from either the American Cyanamid or FP type of air electrode. They consisted of a fine burnished nickel

screen, one side of which was covered by a thin porous membrane. the other side (the active side), contained the platinum catalyst. Two loadings of platinum were tested, these were: 13 mg Pt/in^2, and 58 mg Pt/in^2. Figures 4 and 5 show polarization and capacity data, respectively, for the electrodes. No significant differences were observed between the high and low loading at moderate current densities. It was further found that a cellulosic membrane was not needed for flooding prevention on discharge. An investigation of low temperature performance has been started but not as yet completed.

A study of the American Cyanamid and Chem-Cell Corp. electrodes in other electrolyte systems has also been initiated. Of particular interest is the performance data in perchlorate electrolytes, which, to date, have been found the most successful for the magnesium-air couple with the YEC electrodes. It was found that the American Cyanamid and Chem-Cell platinum electrodes exhibited poor performance in the perchlorate solutions. Although the initial polarization and discharge characteristics were comparable to those of the FP electrode, the performance rapidly deteriorated as a function of discharge time and wet stand. Reference electrode measurements verified that the air electrode was being polarized. The results are shown in Figure 6. It was observed that after one discharge in perchlorate that the electrodes (Chem-Cell and American Cyanamid) were no longer useable. That is, the active material had been removed from the current carrying screen on both types of electrodes.

5.2. Effect of Dry Stand on Air Electrode Performance

An investigation of how prolonged dry stand effects the FP and FSC air electrodes has been started. The experimentation used in this study was set up in the following manner: Polarization data were taken on a zinc-air cell system using freshly prepared platinum and silver catalyzed air electrodes. Each of these electrodes was then washed clean of KOH, dried, and put in a dust free container which was left open to the atmosphere at room temperature. A third electrode, an FSC type, was sealed in a polyethylene bag and placed in the same container. After two months, all electrodes were again tested as above. This experiment will be repeated on a two month cycle for a period of one year. The data of the first test cycle on this regime are displayed in Figure 7.

The activity of both electrodes after a prolonged stand had been lowered. This effect is greater for the silver activated air electrode. During a 50 hour rate discharge the cell voltage was reduced approximately by 10 percent of the original value. For the FP electrodes, however, this reduction amounted to only three percent. A minimum loss of activity on stand was found to occur on the electrode stored in a sealed polyethylene container. No increase in polarization of the air electrode at current densities up to 500 mA/in^2 was noticeable. The greater polarization obtained at high current drains, above 500 mA/in^2, indicated a possible reduction in the activity of the silver. A more significant analysis cannot be made until the testing progresses further. However,

it does appear that air electrodes will not lose their activity in dry cells during prolonged stand if they are stored in a hermetically sealed container.

5.3 Zinc-Air Cells

The experimental work for the development of a zinc-air battery system has proceeded along several distinct and related courses during the second quarter of work. The first was to determine performance after activation at high temperature (120°F). The second was to complete the experimental investigation of heat transfer characteristics and air spacing as a function of temperature and current density, from -25 to 125°F. Finally, the first large size (25 Ampere-hour) cells have been assembled and tested at several current densities at room temperature. The above studies are detailed below:

5.3.1 High Temperature Performance Characteristics

The test cell cases used for this high temperature experimentation were the same as those described in the first quarterly report.

The test cells were fabricated with two layers of Pellon (2506K) and one layer of cellulose adjacent to the cathode. They were then activated with 31% KOH and placed in an oven. The data in Figures 8 and 9 show that the cell characteristics immediately after activation at high temperature are equivalent to those obtained at room temperature. It can be seen that without the cellulosic membrane, there were no flooding tendencies.

The electrolyte, 31% KOH, was chosen for two reasons. This concentration of KOH gives optimum performance at low temperature because of its low resistivity and freezing point. Since a single power system is desired which performs throughout the entire temperature range, it is desireable to keep cell fabrication constant. Also, the solubility of ZnO in 31% KOH has been found by Dirkse* to decrease at 120°F, whereas the solubility of ZnO in higher concentrations increases. This property is desirable because when the cell is cooled down to room temperature, less ZnO precipitates on the surface of the cathode to impede oxygen reduction. This will be discussed in Section 6.3.4.

5.3.2 Zinc Corrosion

The data in Figure 10 illustrate discharge performance for zinc electrodes containing 1 and 2% Hg at both the C/4 and C/50 rate. The capacity at the C/50 rate is approximately one half that at the C/4 rate for the anode containing 1% Hg. This is partially

* Journal Electrochemical Society, p.159, 1959.

due to loss in capacity caused by the higher zinc corrosion rate. This corrosion can almost be eliminated by increasing the mercury percentage to 2%. This is evident by an increase in the capacity obtained for the cell discharging at the C/50 rate. At the C/4 rate a large improvement is not obtained because corrosion effects are less marked during short periods of time.

5.3.3 Air Flow Stoichiometry

The major loss in capacity at the 50 hour discharge is due to carbonation of the air electrode, and loss of water from the electrolyte by evaporation. Both are enhanced by the greater quantity of air flowing passed the cathode surface relative to the stoichiometric requirement at high temperature as compared to room temperature values.

Two types of cell configurations showed poor performance: Cells which were discharged with the air electrodes completely exposed to the atmosphere, and cell systems which had the correct air spacing for high discharge rates (i.e., .100"). Electrode carbonation was noticeable as a white growth on the gas face of the cathode. These crystals block the pores and cover the active surface of the electrode, reducing the diffusion rate of oxygen through the electrode to the catalytic surface. The removal of water by evaporation increases the resistivity of the system and results in a precipitation of ZnO on the active face of the air electrode.

The incorporation of a cellulosic membrane with the separating material adjacent to the air electrode does somewhat minimize the degradation of cell capacity resulting from the effects listed above. This can be seen in Figure 11 where all cells were fabricated with a wetting control membrane and a 100 mil air spacing. The cell with the optimum anode (2% Hg), delivered only 60-70 percent of room temperature capacity at the 50 hour rate. It has been found that minimizing carbonation and water loss enables the cell to deliver full capacity. This is accomplished by controlling the air flow past the air electrode (i.e., reducing the air spacing).

Figure 11 shows performance at the 2C, C, C/5 and C/50 discharge rates for zinc-air cells with 100 mil spacing (at an ambient temperature of 120°F). The capacities for the test cells at the C/4 and higher rate averaged 2 Ampere-hours. At the C/50 the capacity was 1.2 to 1.4 Ampere-hours. By reducing the size of the air vents from 100 to 25 mils (at the C/50 discharge rate), capacity was considerably improved. These results are illustrated in Figure 12.

Work completed during the first quarter indicated that the critical air spacing, that is, the air spacing for which there is a consirable voltage and capacity dependence, is in the range of 10 mils. at the C/50 rate. The minimum air spacing for optimum cell per-

formance is one which allows close to stoichiometric air flow as required by the discharge, without increasing carbonation and water loss or decreasing heat transfer.

The extension of this functional parameter to other discharge rates and temperatures will be examined in the next quarterly report.

5.3.4 Effect of Activated Stand on Cell Performance

Data are presented which show that activated shelf life can be increased by (1) incorporation of a cellulosic membrane adjacent to the cathode, (2) sealing the cell from the atmosphere, and (3) by use of a "parasitic" discharge drain.

The most severe conditions that an activated battery would have to meet during a shelf stand would be at the high end of the temperature range, that is, about 50°C. This is where performance is greatly decreased.

Exploratory work on activated shelf life has been started during this quarter. Zinc-air cells with FSC air electrodes were fabricated, activated with 35% KOH, and placed in a controlled temperature oven at 50°C. The separator system consisted of two layers of 10 mil Pellon and one cellulosic membrane. The cells which were not in sealed polyethylene bags had their air electrode faces completely exposed to the air. A discharge after 24 hours showed that the performance of the unprotected cells deteriorated quite severely. At 1 Volt, the cell delivered only 100 mA/in^2, as compared to 400-500 mA/in^2 at one Volt obtained from the cell discharged immediately after activation. The excessive polarization was caused by evaporation of water from the electrolyte, which resulted in drying out of the separating material, which in turn lead to excessive carbonation. It can be seen from Figures 13 and 14 that the cells which were stored in sealed polyethylene bags maintained their original characteristics, except for a slight lowering of the polarization curve.

When the cells were allowed to cool to room temperature after wet stand at high temperature, the cell voltage and capacity were greatly decreased. From reference electrode measurements it was found that the poor performance was associated with increased polarization on the cathode. During the high temperature wet stand, the self discharge of the zinc anode saturated the electrolyte with zinc oxide. On cooling, the solubility level was lowered enough to cause precipitation of ZnO in the pores of the air electrode. Data given in the literature* indicates that the concentration of the zincate phase in saturated solutions of ZnO in 31% KOH has a smaller temperature dependence than in 35%KOH. Two cells with the same construction were activated with 31 and 35 percent KOH respectively. After a 48 hour wet stand at 50°C, the cells were discharged. The data are presented in Table I. It can be seen that decreasing the KOH concentration gives a higher limit-

* T. P. Dirkse: "Composition and Properties of Saturated Solutions of ZnO in KOH; 5. Elec. Chem. Soc., V 106, 154-5.

ing current density when the cell is cooled.

TABLE I

KOH CONCENTRATION AT HIGH TEMPERATURE CURRENT DENSITIES
Given for cell voltage at one Volt

TEMPERATURE	31% KOH	35% KOH
50°C	295 mA/in^2	310 mA/in^2
25°C	130 mA/in^2	25 mA/in^2

It should be noted that data given in this Table are for short duration wet stands of two days or less. At present it appears that incorporation of the optimum methods of cell fabrication which have just been discussed (i.e., 2% Hg amalgam, cellulosic membrane, hermetic sealing, and 31% KOH), will not give a cell which can maintain its initial properties for any longer periods of time at elevated temperatures.

The good performance during a 50 hour discharge at 120°F already illustrated indicates that cell capacity can be completely maintained for at least a two day period. Cell performance could possibly be preserved for a longer period of time by the same method, simply by reducing the discharge rate. For a longer discharge the air flow passage must be reduced to a value corresponding to the current density.

In the first report it was postulated that the tendency to flood on stand may be due to a formation of a thin film of $Pt(OH)_2$ or Ag_2O on the catalyst's surface at the reversible potential. Such a film would have a higher wetability and would promote the passage of liquid through the cathode. On discharge, however, the film would be reduced, so that the tendency to flood would be decreased. Bockris, et-al*, showed that platinum sheet developed an oxide film immediately after immersion in alkaline solutions. The films were about 7Å thick. The thickness of the oxide was found to increase to 19Å after about 20 hours at the rest potential. It was further found that when the sheet was negatively polarized about 50 mV, the oxide layer was reduced. Theoretically, then, a cell discharging at the one year rate, would, after six months, deliver about 50% of its original capacity at a voltage level e-

* Reversible Oxygen Electrodes, Report #12 USAEL, Dec., 1964. Contract No. DA36-039SC-88921.

quivalent to the one obtained immediately after activation. An investigation of this parasitic drain technique has been started and will be completed next quarter. The results to date are presented below:

Two cells were fabricated with standard zinc electrodes, platinum cathodes, 2 layers of Pellon (2506K) and one layer of cellulose next to the air electrode. They were activated with 31% KOH, and a 12.5 mil air vent opening was used to allow only limited air flow past the cathode. The cells were then subjected to a continuous parasitic drain of 0.4 mA/in^2 (C2000 rate) for one month. Reference electrode measurements taken during this period showed about 30 mV polarization on the air electrode. The cells were then discharged at the C/4 rate and they yielded about 60% of the theoretical capacity with no decrease in voltage. In fact, the loss in capacity corresponded to the consumption of zinc during the parasitic drain. Further work will be done during the next quarter to determine the lowest current rate which will prevent flooding. This value undoubtedly will also be a function of temperature. The possibility that the mechanism involved in the reduction of flooding is electrophoretic rather than electrochemical will also be investigated.

Another technique for maintaining shelf life is to store the cell, after activation, in a closed container which has been scrubbed free of oxygen with nitrogen. For field operation however, this method would last only till the time of the cells first use. After a partial discharge, the cell can be returned to an equivalent dormant state by sealing and then discharging it through a resistor until all oxygen in the closed system is consumed.

5.3.5 Long Duration Discharges

Already discussed in the high temperature section was the fact that full capacity at 50°C can only be obtained by limiting air flow to the minimum value essential to obtain the stoichiometric quantity of air. This is particularly true at the C/50 rate discharge. Also, at room temperature and 0°C, the reduced air flow results in a 5 to 10% improvement in capacity. At lower temperatures (i.e., -30°C), there is no apparent improvement by keeping air flow to a minimum. Figure 15 shows 50 hour discharge performance for cells with the optimum cell fabrication (a 10 mil air spacing), at various temperatures. It should be noted that the high and medium temperatures (+50, +25, 0°C) work used anodes with a Zn density of $2 g/cm^2$ and a 2% Hg amalgam. At -30°C the zinc anode was pressed to a density of $1.8 g/cm^3$ and had been treated by the C.W.T. method (described in the first quarterly report). The capacity improvement, at low temperature affected by this process at -30°C is shown in Figure 16.

5.3.6 25 A.hr Zn-Air Cell

In anticipation of future breadboard models to be delivered at the end of the contractual period, test cells of 25 hour capacity were fabricated. The zinc plate was utilized on both faces, as opposed to the zinc plates in the original test cells, where only one face of the zinc was discharged. The dimensions of the active pack were:

Anode: 1/Cell

4.75" x 6" x .046"

37.5 g. Zn/PLT + 2% Hg DOFL treated

Zn density = 1.8 g/cm^3

Cathode: 2/Cell

Ag or Pt type

4.75" x 6" x .010"

Leads: 1 x 1/8" Ag TAB.

Separator: 2 Pellon bags (Pellon thickness = 10 mils).

Dimensions of Single Cell Pack:

	Thickness	Weight
1 Zn	.096 inch	45 grams
2 Air Electrodes	.020 "	34 "
2 Pellon Bags	.040 "	4 "
	.106 inch	83 grams

Electrolyte (31% KOH) 35 cm^3/cell = 46 gram/cell

Cell Volume (Active Pack) = 4.75" x 6" x .106" = 3.02 in^3

Cell Weight (Active Pack) = .286 lb. (129 g).

The cell cases were constructed with .075 inch lucite material making the total thickness of the individual cell about .125". Initial work was done with single cell units. Lucite plates were attached to each air electrode with a 100 mil air spacing. Performance data as a function of discharge rate for the 25 Ampere-hour cells using the Chem-Cell Corp. platinum electrodes are shown in Figure 17. Discharge data at high and low rates for the YEC FP and FSC air elec-

trodes are illustrated in Figures 18 and 19.

It should be noted that these cells were run individually. To simulate a battery discharge, three cells were assembled in series. This was done to determine the thermal characteristics on discharge. This particular phase of study will be discussed later in the heat transfer section. Table II gives energy density for FP and FSC electrodes at the C and C/50 rate of discharge.

TABLE II

ACTIVE PACK ENERGY DENSITY FOR 25 A.hr CELLS

	C		C/50	
FP	97 wh/lb.	9.2 wh/in^3	115 wh/lb	10.9 wh/in^3
FSC	88 "	8.35 "	110 "	10.4 "

5.4 Magnesium-Air Cells

An investigation of the magnesium-air system has been initiated during this quarter. The outstanding problems associated with improving performance are: (1) developing an electrolyte which will minimize magnesium corrosion, (2) which is also compatible with the cathode, and (3) which does not freeze at -25°F. To date, one electrolyte which meets the first two requirements has been found. The electrolyte and anode-cathode systems studied are discussed in the following sections.

5.4.1 Magnesium Anode Corrosion

The polarization apparatus (described in the first quarterly report), has been used during this quarter to measure corrosion rates of magnesium in $Mg(ClO_4)_2$, $Mg(Ac)_2$, and $Mg(BrO_3)_2$ electrolytes. This apparatus, with most of the accessories, is pictured in Figure 20. It is designed to measure active material utilization during the anodic polarization of a known quantity of metal. The metal electrode under test is suspended on a stainless steel shaft in the large anodization chamber. The active face of this electrode is orientated toward the carbon cathode in the opposite smaller chamber. The auxiliary chamber, positioned at 60° to the carbon cathode chamber, contains a reference electrode compatible with the particular electrolyte. The discharge current is supplied by an outside constant current D.C. power source and the anodic potential is measured against the reference electrode using a Leeds & Northrup K-3 potentiometer. An eudiometer (pictured to the left of the apparatus), measures the volume of the gas evolved from the anode during the discharge. The experimental test procedure is described below.

The anode material is first machined to a well defined area (± 1%). Then all edges not to be utilized during the anodization are coated with epoxy. The dimensions of the active anode are 1 x 1 x .08 cm. The magnesium anodes tested were, in all cases, were AZ61 . After the anode is properly fastened inside the closed anode chamber the internal pressure is equilibrated to 760 mm Hg and the initial volume is recorded. A discharge current is then applied for a period sufficient for the evolution of about twenty five cubic centimeters of hydrogen. The total weight loss of the magnesium anode is calculated as the sum of the applied and local corrosion currents. The local corrosion current is determined from the volume of hydrogen which is the difference between the initial and final volume readings. Both readings are taken after the equilibration of internal pressure to atmospheric pressure. All potential readings were measured against the standard calomel electrode.

Evaluation of the polarization data accrued by the above technique was done by computing the data in terms of corrosion current density and coulombic efficiencies as a function of current density. The corrosion current density is equal to the volume of hydrogen evolved at ambient temperature and pressure, divided by the time of the test and the area of the anode, and multiplied by the appropriate dimensional constant. The equation is given below:

$$\text{Corrosion Current Density} = \frac{(k)(\Delta V)}{(\Delta t)(\ A)}$$

The coulombic efficiency is the applied current divided by the sum of both the coulombic and corrosion currents. Table III gives these data for the electrolyte tested. Corrosion current densities for these electrolytes are shown in Figure 21.

TABLE III

ANODIC DISSOLUTION OF MAGNESIUM

Electrolyte	Open Circuit Corrosion mA/in^2	APPLIED CURRENT DENSITIES 64 mA/in²	129	258	516	1032
$Mg(ClO_4)_2$	30	67%		66%	70%	70%
$Mg(ClO_4)_2$ & 1% NaCl	100	64%	67.3%	68.2%	70%	69.5%
$Mg(BrO_3)_2$ & 1% NaCl	Not available			71%	76.8%	73.2%
$Mg(Ac)_2$ & 1% NaCl	5	62.4%	64%	71%	63.4%	60%

The coulombic efficiency of the magnesium anode in 3N $Mg(ClO_4)_2$ is about 65-70% of theoretical, while for $Mg(Ac)_2$, 3N, it is about 60-65%. Although $Mg(Ac)_2$ has a poorer coulombic efficiency, it is apparent that it has a substantially lower corrosion rate at the reversible potential as compared with $Mg(ClO_4)_2$. The 2N $(Mg(BrO_3)_2$ solution gave coulombic efficiencies in the range of 70-75%. However, in the experiment for the determination of the open circuit corrosion rate, the $Mg(BrO_3)_2$ solution dissolved the protective layer of potting, exposing all sides of the anode, thus increasing the total volume of hydrogen evolved and therefore rendering the corrosion data invalid. This particular experiment will be re-run during the next quarter of work. It is expected that the O.C.V. corrosion rate of this electrolyte will be in the range of that of $Mg(ClO_4)_2$ since its pH is also in that range. See Table IV below:

TABLE IV

pH OF MAGNESIUM-AIR ELECTROLYTES

Electrolyte	pH
3N $Mg(Ac)_2$	8.4
2N $Mg(BrO_3)_2$	6.7
3N $Mg(ClO_4)_2$	6.0

The voltage-current density characteristics have also been determined for magnesium in the above electrolytes. The polarization data are shown in Figure 22. The variation in voltage among the electrolytes is small, except for magnesium in $Mg(Ac)_2$ at high current densities. This could be explained by the low conductivity of this weak acid salt. Figure 23 shows the voltage-capacity characteristics for magnesium in the various electrolytes tested.

5.4.2 Magnesium-Air Cell Tests

During the first quarter of work it was found that under the particular test conditions the consumption of water by the magnesium corrosion reaction dried out the cell system which resulted in poor performance. The dry separator material undoubtedly inhibited mechanical "washing" of the magnesium oxide from the surface of the anode and therefore caused rapid polarization. During this quarter a free electrolyte system was employed which eliminated this problem. In the test cells the spacing between the opposing electrodes was set arbitrarily at .150". Controlled experiments which will determine the optimum inter-electrode spacing however, have not been finished yet.

The magnesium (free electrolyte) air test cells described above exhibited several problems. One difficulty encountered was the gradual polarization of the air electrode. This was particularly evident in the case of pure magnesium perchlorate electrolytes. It was found that immediately after activation with the magnesium perchlorate electrolyte, that a pulse of 50 mA/in^2 gave a cell voltage of 1.2 V. However, the voltage rapidly deteriorated to less than .6 V. in a few minutes. Reference electrode measurements showed that the entire polarization was occurring on the air electrode. Apparently this was a result of precipitation of $Mg(OH)_2$ in the pores. Polarization was found to markedly decrease however, by introducing a small percentage of NaCl to the supporting electrolyte. Figure 24 shows polarization data for a Mg-air cell activated with a $Mg(ClO_4)_2$ and NaCl electrolyte. The $Mg(ClO_4)_2$ was 3 N and NaCl was added to give a 1:5 ratio of Cl^- to $Mg(ClO_4)_2$. The data for 3 N $Mg(ClO_4)_2$ without NaCl showed that no plateau voltage was obtained during discharge; this was due to rapid cell polarization. The cell with NaCl , however, exhibited a fairly flat voltage plateau.

The electrolytes tested in the corrosion test were also studied in magnesium-air cells. Polarization data at room temperature are given in Figure 25.

Discharge data for the $Mg(BrO_3)_2$ and $Mg(ClO_4)_2$ electrolytes are illustrated in Figures 26 and 27. Also included in Figure 26 are discharge data for a cell containing 3N $LiBrO_3$. A more complete investigation of the lithium salts, including $LiClO_4$ will be conducted during the next quarter of work.

The magnesium-air system which gave satisfactory performance at room temperature did not operate in the low temperature region. A prerequisite for low temperature operation is that the electrolyte maintain fluidity at the low end of the temperature requirement (i.e., -25°F). Five normal magnesium perchlorate and acetate solutions with sodium chloride meet this requirement. However, a saturated $Mg(BrO_3)_2$ solution froze at -25°F.

A low temperature investigation of the Mg-air couple in perchlorate has also indicated that its increased viscosity (see Table V) drastically reduces the mobility of hydroxyl ions in the solution and/or reduces the reversibility of one or both of the electrodes.

TABLE V

PHYSICAL PROPERTIES OF $Mg(ClO_4)_2$ SOLUTIONS

$Mg(ClO_4)_2$	Temperature	Absolute Viscosity	Density
3N	23°C	1.37 centipoises	1.17
4N	23°C	1.48 "	1.23
5N	23°C	1.76 "	1.30
5N	-27°C	5.05 "	1.30

During the next quarter of work polarization data will be obtained at low temperatures for the magnesium and air electrodes in the apparatus described in Section 5.4.1.

5.4.3 Specific Energy Calculations for the Mg-Air System

Approximate calculations of specific energy for the active materials used in this investigation were made. The test cells utilized both sides of a 31 mil magnesium (AZ61) sheet. The individual faces were 1.55 in^2 and the weight of magnesium discharged was 1.40 g. The volume of the electrolyte was 7.6 cm^3 which weighed 9.0 g. Weight of air electrodes were 3.2 g. Therefore, the total weight of the active components was 13.6 g. or .030 lb. Table VI gives specific energy using the discharge performance from Figure 27.

TABLE VI

SPECIFIC ENERGY FOR Mg-AIR TEST CELLS

I.D.	Specific Energy
65 mA/in^2	55 Watt-hr./lb.
130 mA/in^2	51.5 Watt-hr./lb.

This data shows that the present construction does not appear favorable to achieve a high energy density system. Also, it should be remembered that in comparison, the zinc-air watt.hr/lb. calculations for the same size cell geometry gave over 150 watt.hrs./lb.

Two methods for improving the performance will be investigated next quarter. They are: (1) increasing the magnesium thickness (i.e., weight) per cell and (2) reducing the volume of free electrolyte. A double thickness of magnesium anode giving a similar discharge curve as shown in Figure 27 at the 65 mA/in^2 rate, will deliver a 101 watt-hr./lb. Adding to this the possible improvement realized by a one-third reduction in the volume of electrolyte (100 mil inter-electrode separation instead of 150 mil), the watt.hr. efficiency for the active material becomes 140.

5.5 Aluminum Electrode

The search for an electrolyte which would be compatible with an aluminum anode and an air electrode is under investigation in this phase of the program. Specifically , the investigation during this quarter included a study of several aqueous electrolyte systems. KOH solutions (25-35%) with various percentages of $NaAlO_2$ and ZnO were tested. Sodium chloride and NH_4Cl additives to alkaline electrolytes were also studied. The complex ions of aluminum and zinc improve the anodic dissolution properties of aluminum while the chloride salts are added to prevent polarization on the cathode. A ternary electrolyte system consisting of 12% $ZnCl_2$, 15% LiCl, 8% NH_4Cl and 65% H_2O was also examined. The separator material used in these test cells was 3 folds of absorbent Pellon wrapped around 99.9% purity aluminum anodes. The cathode was the FP type. Table VII presents performance data for these electrolyte systems.

The aqueous electrolyte solutions with K^+ and OH^- as the principle ionic species (35% KOH) gave poor performance on discharge. In this electrolyte no plateau voltage was obtained during moderately high rate discharges (i.e., C/4).

TABLE VII

PERFORMANCE OF VARIOUS ALUMINUM-AIR ELECTROLYTE SYSTEMS

Electrolyte (Aqueous Solution)	Cell Voltage (at I.D.=123mA/in^2)	Capacity Withdraw (Amp.-hr./Cell)
35% KOH, 8% $NaAlO_2$	.76	-
35% KOH, 4% $NaAlO_2$	1.09	-
35% KOH, 4% AlO_2, 1% NaCl	.80	.05
25% KOH, 4% $NaAlO_2$, 3% NaCl	1.26	.15
35% KOH, 8% ZnO	1.00	.05
35% KOH, 4% ZnO	1.03	.06
20% KOH, 4% ZnO, 12% NaCl	1.15	.20
25% $AlCl_3$, 4% NH_4Cl	.58	-
12% ZnCl, 15% LiCl, 8% NH_4Cl	.41	.10

The KOH-ZnO electrolyte gave a short plateau voltage during discharge at the same rate. It was thought that the voltage plateau obtained was due to zinc discharging at the surface of the aluminum. The zinc, of course, was formed by replacement plating with aluminum. To determine the validity of the above hypothesis, pre-weighed aluminum anodes were first soaked in a zincate solution. The anodes were weighed after treatment to determine the quantity of zinc deposited. The electrodes were then fabricated into cells and activated with 35% KOH and 4% ZnO electrolyte. The cell voltages determined as a function of discharge current density were similar to those recorded for zinc-air cells. The capacity of the length of the discharge plateau voltage was directly related to the amount of zinc deposited on the surface of the aluminum. It was concluded that an aluminum-air cell using a zincate additive in the electrolyte exhibited initial performance that was characteristic of a zinc-air cell. However, after the zinc was consumed the cell polarized quite rapidly.

Electrolytes tested which were more compatible with aluminum included lower concentrations of KOH (25% KOH) with $NaAlO_2$ and NaCl additives. Figure 28 illustrates the improvement in polarization obtained by the reduction of KOH concentration and addition of NaCl. However, only 10% of the capacity requirement per unit area of anode surface has been reached.

A moderately favorable electrolyte was the ternary system mentioned above. Although the air electrode gave poor polarization characteristics in the electrolyte, the aluminum anode behavior was more favorable than with the alkaline electrolytes. Another advantage of this electrolyte is its relatively low pH.

rawn
11)

The performance characteristics in aluminum-air cells might be improved by alloying. Attempts to obtain aluminum alloys (coded MRLAG and MRL 12226) prepared by Olin Mathieson for exploratory studies have been unsuccessful. The important component of these alloys is .1 to .2% tin. During the next quarter additional attempts will be made to obtain the above alloys.

Investigation of a free electrolyte system for aluminum as opposed to cells using a bibulous separator material will be done during the third quarter. This alteration in the physical structure could, as in the case of Mg-air, greatly improve the performance. In conjunction with this possible improvement, gassing rates and polarization data in free electrolyte will be studied using the polarization apparatus previously described.

5.6 Barium Electrode

A limited study of the barium anode is scheduled for the third quarter. Barium strips of 20 mil thickness have just been obtained from Pfizer Metals Co.

At present the feasibility of a barium-air system based on the studies conducted during the first quarter appears quite unfavorable. Extremely high gassing rates were evident in high pH solutions (35% KOH), even with $ZnO_2^=$ and $CrO_4^=$ inhibitors.

The study of barium during this quarter will include various alcoholic-KOH solutions with various inhibitors to reduce electrode gassing. Possible decreases in gassing rate by surface annealing of barium will also be investigated.

Calcium Electrode

The preliminary investigation of calcium, conducted during the first quarter, indicated that the use of uninhibited alkaline electrolytes was not feasible. In such a media the calcium anode forms a continuous oxide film resulting in complete polarization.

A more intensive investigation of this anode is scheduled for the third quarter. This study will include predominantly inhibited electrolyte systems with relatively low alkalinity. The chief problem encountered with this approach will be compatibility with the air electrode. The cathode must have a partially aqueous media for efficient reduction of oxygen. Since calcium has such a high electro-negativity, it will react with almost any aqueous electrolyte. At present it is known that solutions that contain a miscible organic solvent and water reduce the gassing rate without seriously damaging the air electrode performance. This corrosion might be further reduced by increasing the overpotential of hydrogen on the anode by alloying with other metals. Calcium sheets with 1% alloys of tin, zinc and lead have been ordered from Pfizer Metals Co. They will be examined in electrolytes found to be the most compatible with both electrodes.

5.8 Metal-Air Battery System

During the first quarter, studies were begun to establish the best design parameters for a multi-cell metal-air battery. The most important parameters are the spacing between the air electrodes of adjacent cells and the particular cell geometry (i.e., surface area of cathode exposed to the air). It is these dimensions which dictate the rate of air flow past the air electrodes.

At very low rates an adequate supply of oxygen can be supplied by diffusion. The upper rate for the diffusional supply of oxygen is dependent upon the physical configuration of the battery. At discharge rates which consume oxygen faster than this upper limit for diffusion, air convection flow resulting from temperature rise is desirable. This convection will supply fresh air to the cathode. The limiting temperature rise for a particular cell configuration in a battery will be a function of the inter-dependence between cell voltage, air spacing and current density.

At present some consideration has been given to the design for the exploratory development battery. With regard to air flow, the most favorable method for adjusting air flow will be by manually controlling the vent port for the battery. The individual cell cases would be permanently fastened in position with an inter-cell spacing sufficient to allow for an adequate air flow at the highest discharge rate.

At the highest rate of discharge the air ports would be opened to the maximum position. For other discharge rates and ambient temperatures, the air ports would be adjusted to give optimum performance. For example, at low discharge rates with negligible battery temperature rise, the air supply would be kept to the minimum amount necessary to maintain the maximum voltage. This would be accomplished by having the vent ports opened to the minimum aperture. The necessity of this has already been discussed in the high temperature work described in section 5.3.1. For a high rate discharge at low temperature, air vent control is necessary for "bootstrap" operation. This would consist of briefly short circuiting the battery terminals with air ports adjusted to maintain the highest current at a minimum voltage. Once this operation has increased the internal temperature of the battery, the air ports are opened completely and the unit is ready to supply the desired energy.

5.8.1 Air Flow Requirements

The first quarterly report detailed the experimental procedure used to determine cell discharge performance as a function of air flow. Briefly, the investigation consisted of discharging test cells with

12.5, 25, 50 and 100 mil wide apertures. The sides of the cells were sealed to allow only vertical air flow. The temperature rise of the cell was monitored by a thermocouple. The cell packs for these experiments used low density zinc anodes (2% Hg amalgam for high temperature and C.W.T. treated for low temperature), 20 mil absorbent polyamide separator, and an FP cathode. They were activated with 31% KOH. The experiments were carried out at room temperature and 32°F. At 120 and -25°F only the test cells with 100 mil wide air vents were discharged. During the C/50 rate discharge at high temperature, however, 12.5 mil wide spacing was necessary to obtain full capacity.

Cell performance as a function of air flow has not been fully analyzed yet. After air flow data has been obtained for the larger 25 Ampere-hour Zinc-air cells, a complete analysis will be presented. This study will probably be completed during the third quarter of work.

Heat flow calculations have been completed for four temperatures. The computations consisted of determining the K-value in the simplified heat transfer equation for small vertical surfaces. The equation,

$$h_c = k\left(\frac{\Delta T}{L}\right)^{\frac{1}{4}} \Delta T$$

where:

h_c = B.t.u./hr.f_L^2

t = Temperature difference between vertical surface and fluid in degrees Farenheit.

$$\frac{1}{L} = \frac{1}{L_{vert}} + \frac{1}{L_{horz}}$$

where:

L_{vert} is the vertical length and L_{horiz} is the horizontal length in feet.

K = A dimensional constant dependent upon the viscosity, density, specific heat and conductivity of the surrounding fluid,

gives the heat flow from a vertical surface as a function of temperature rise and plate dimensions to a surrounding fluid at constant temperature. For air at room temperature and ambient pressure, K is .29. This, however, is for a single vertical surface, whereas the test cells used consisted of two adjacent surfaces at a spacing

of 100 mils. This restriction makes the above K value invalid. Consequently, instead of calculating the h_c value from temperature data, the h_c value was calculated from the plateau voltage during discharge at a particular discharge rate. This was then substituted into the given heat flow equation to calculate the K values. The results of these calculations are given in Table VIII.

TABLE VIII

HEAT FLOW CALCULATIONS

Ambient Temperature °F	Discharge Rate mA/in^2	h_c B.T.u./hr.ft^2	T °F	K	Average K
120	820	185	58	.74	
120	410	33.5	12	.79	.72
120	164	12.4	6.3	.65	
75	820	140	54	.52	
75	410	110	40	.66	.63
75	164	13.5	5.5	.81	
75	16	1.1	Negligible temperature rise.		
0	820	182	47	.80	
0	410	92	31	.68	.73
0	169	67	18	.71	
-25	820	260	62	.82	
-25	410	Not available			.77
-25	164	24.6	12	.72	

The significance of K is that it represents the heat transmission from the heated system to the cooler ambient fluid. A relatively high K value means that a system, for a given temperature difference with respect to the ambient will transfer heat to the ambient at a relatively high rate. Figure 29 gives the theoretical and experimental K value as a function of the temperatue of the surrounding fluid.

It can be seen that the dissipation of heat to the surroundings increases as the ambient temperature is reduced. This functional theoretical dependence is also followed by the experimental data obtained. The first interpretation of the data with a view towards development of a full size metal-air battery, is that some difficulties may be encountered in low temperature bootstrap operation. However, the increased inefficiency on discharge at low temperature, resulting from higher polarization at both electrodes, (I^2R heating) will result in a greater build-up of heat in the battery.

Modifications of bootstrap heating were partially discussed in the previous section. Decreasing the air flow to increase the inefficiency of the discharge was one method suggested for increasing the heat generation rate. The principles of this tecnnique are illustrated in Figure 30 which shows discharge characteristics for various air vents at a discharge rate of 820 mA/in^2. This rate approaches in magnitude the short circuit discharge current. Also shown are the temperatures of the active packs during discharge. The discharge run at 0°C shows some effect of bootstrap operation. Initially, the cell with a 50 mil wide vent port gave a cell voltage of .5 V. as compared with a voltage of .8 V. for a cell with a 100 mil aperture. Within 10 minutes, the voltage of the cell with the smaller vent had risen to the same value as the cell with the largest opening. At this point its temperature was 18°C compared to 10°C for the 100 mil spacing. This indicates that a more restricted air flow is accompanied by a higher temperature rise. However, there is a limit to which temperature rise is accompanied by a simultaneous voltage rise. For instance, it has been found that a cell with a 25 mil spacing discharging at 820 mA/in^2 increased in temperature to 25°C after two minutes (about 6% of the zinc anode capacity was utilized during this time). The cell voltage improvement accompanying this temperature rise was less than one-tenth of a Volt. If the air aperture had been increased 100 mils after the initial two-minute heating period, the cell discharge performance probably would have been equivalent to the room temperature discharge.

6. Program for the Third Quarter

6.1 Zn-Air

Investigate heat transfer characteristics for larger size zinc-air cells (25 AH capacity) and correlate this data with heat transfer data obtained from the smaller (2.5 AH) test cells.

Determine maximum voltage-current density characteristics for these larger units.

Start multi-cell battery tests.

Determine applicability of parasitic drain techniques for long activated shelf life. Special emphasis will be given to high temperature storage (125°F).

6.2 Mg-Air

The emphasis during the next quarter will be to determine corrosion rates and material utilization for magnesium $Mg(ClO_4)_2$, $Mg(Ac)_2$ and $Mg(BrO_3)_2$. Other perchlorate salts, i.e., $NaClO_4$ and $LiClO_4$, which exhibit the lowest freezing solubility point, will be included in this investigation.

Polarization data for both the magnesium anode and air cathode will be studied as a function of the amount of dissolved anodic material per unit volume of electrolyte.

Based on the above findings, Mg-Air cells will be constructed which will give the maximum watt-hour/lb. efficiency. These cells will be tested over the current density and temperature range of 2C to C/50 and 125°F to -25°F.

6.3 Ca-Air

Calcium anode behavior will be examined in organic-aqueous solutions. Special electrolyte additives, including ammonium and lithium salts, will be tested.

The organic-aqueous media will include alcoholic-KOH solutions and alcoholic ammoniacal salt solutions.

Calcium alloys containing Zn, Sn, and Pb, now on order from Pfizer Metals Co., will be prepared for testing in the electrolytes found most compatible with pure Ca and the air electrode. An investigation of anodic corrosion rates for the calcium alloys in the various electrolytes is also planned.

6.4 Al-Air

Incorporation of a free electrolyte system will be examined. The

electrolytes will include those which at present appear most favorable. The investigation will include determination of corrosion and polarization characteristics.

6.5 Ba-Air

Electrolyte systems similar to the group tested on calcium will be examined in barium-air cells.

Possible improvement by annealing the Ba sheets will be investigated.

7.

APPENDIX

LIST OF KEY PERSONNEL

			No. of Hours
Dr. G. A. Dalin	-	Director of Research, AVP.	35
Allen Charkey	-	Project Engineer	230
Raymond Blossom	-	Chemist	516
D. B. Smith	-	Technician	521
M. Vasu	-	Technician	490

FIGURE 1

PERFORMANCE DATA FOR AMERICAN CYANAMID Zn-Air ELECTRODES

Room Temp.
Id. = 200 ma/in^2

35% KOH
Anode Area = 2.43 in^2
Zn Density - 2.g/cm^3

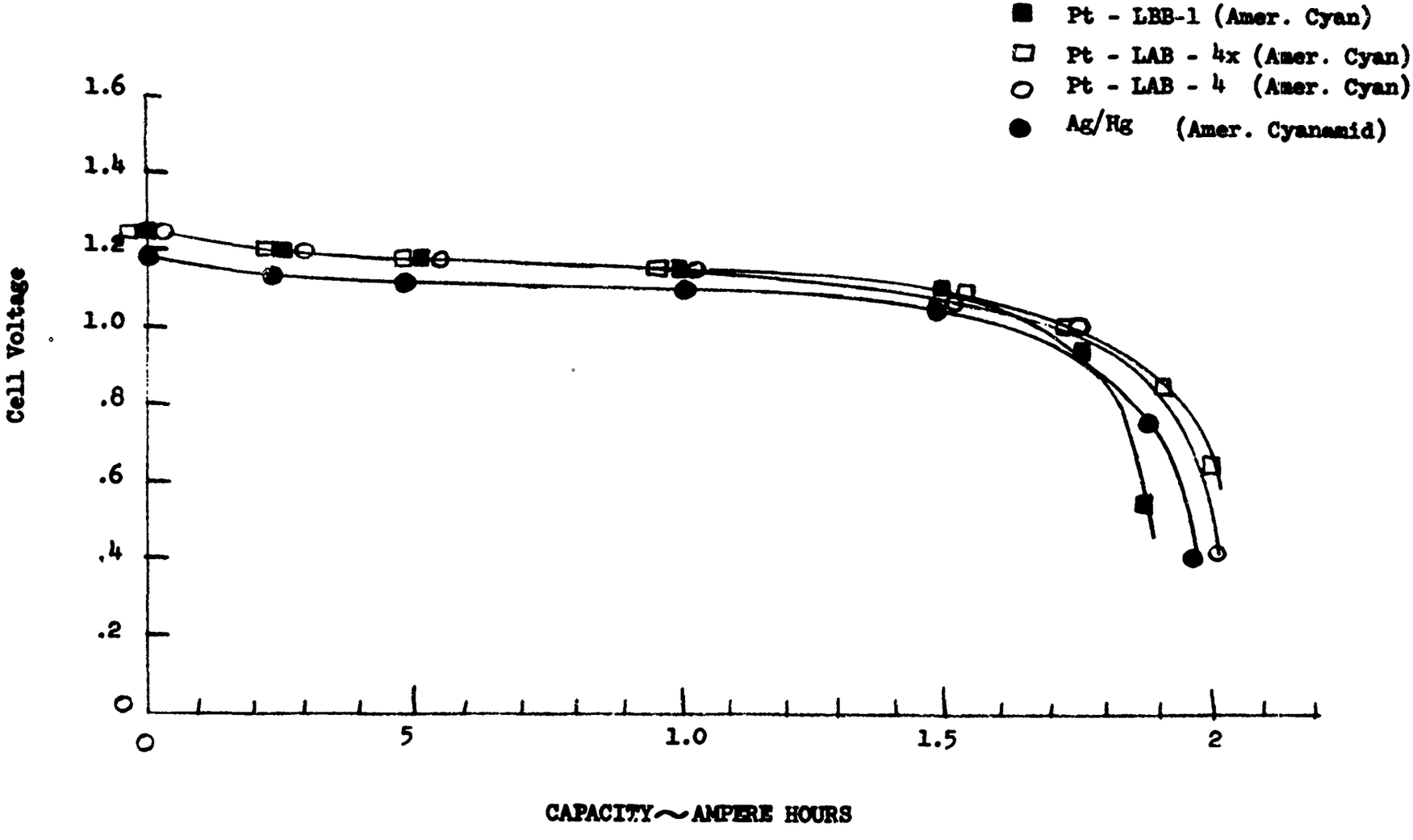
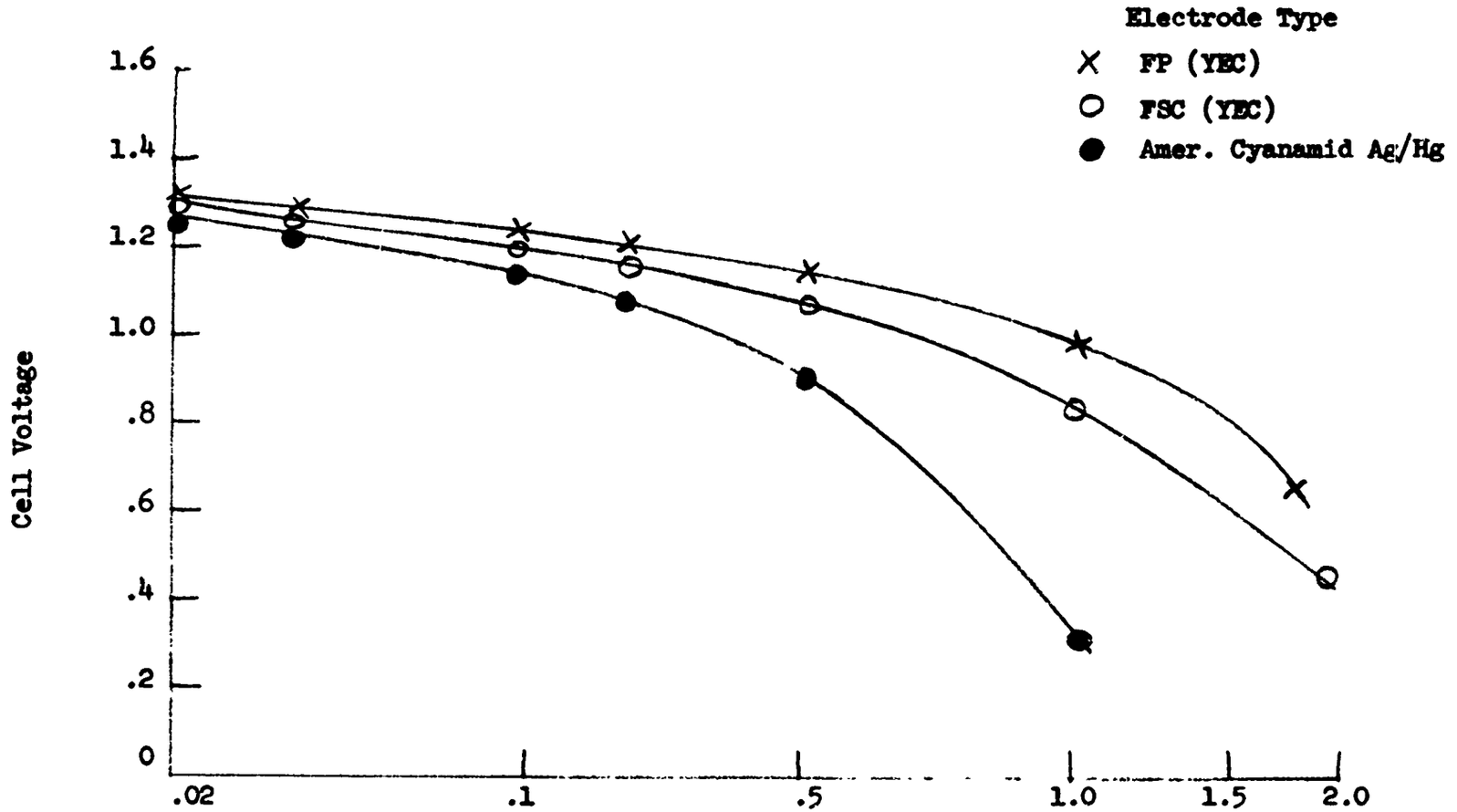


FIGURE 2

AIR ELECTRODE POLARIZATION DATA
Zn - Air

Room Temp.
35% KOH
Zn Density = 2 g /cm^3



DISCHARGE CURRENT DENSITY ~ A/in^2

FIGURE 3

LOW TEMPERATURE DISCHARGE DATA
Zn - Air

Temp = -30°C
Anode Area = 2.43 in^2
Zn Density = 1.8 g/cm^3
Zn Plt. Wt. = 2.2 g
C.W.T. Treated Zinc
31% KOH

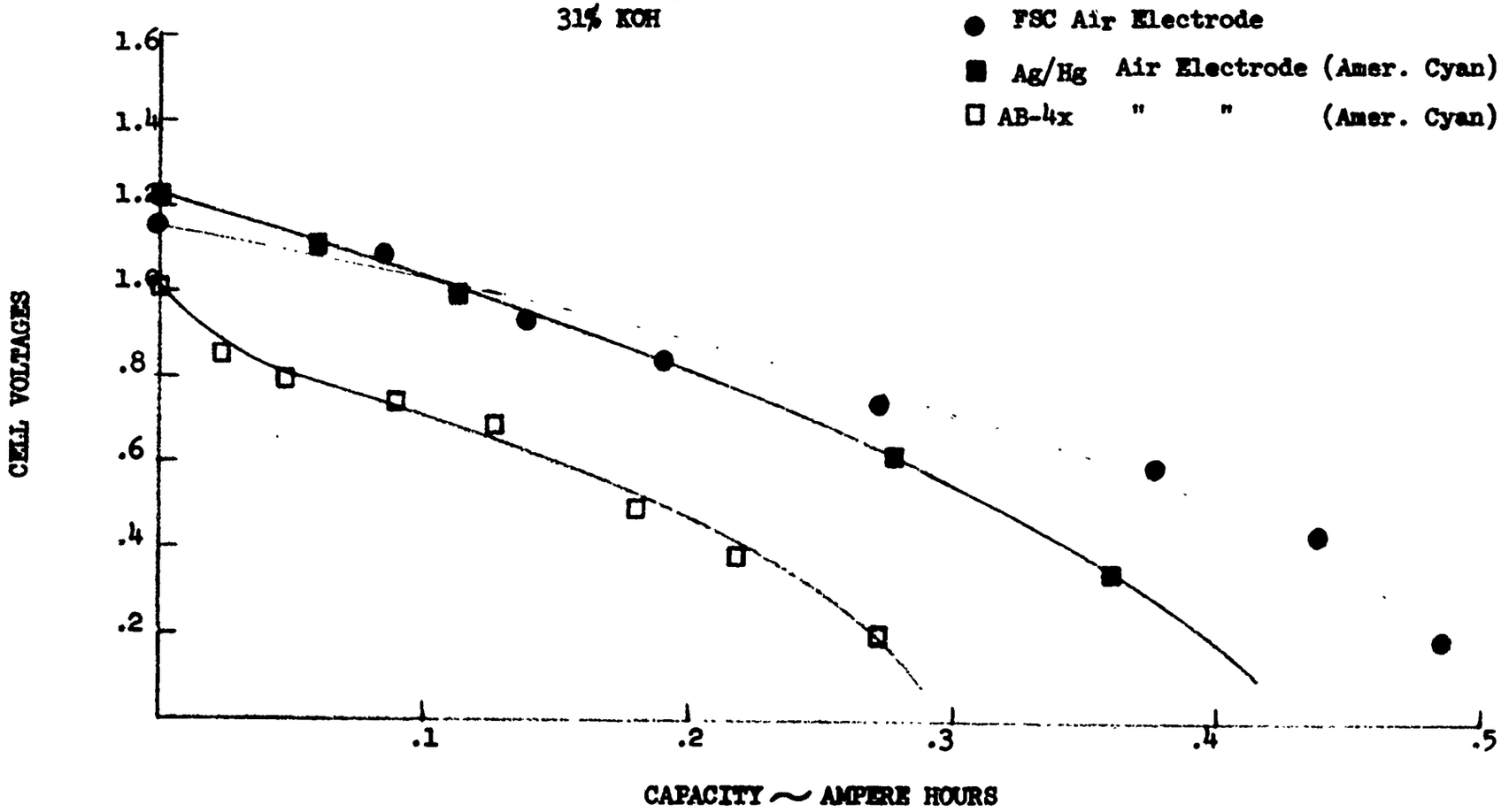


Figure 4

POLARIZATION DATA — Zn-Air
Chem. Cell Air Electrode

Room Temp.
Zn Density = 1.8 g/cm^3
DOFL. Zn.
35% KOH

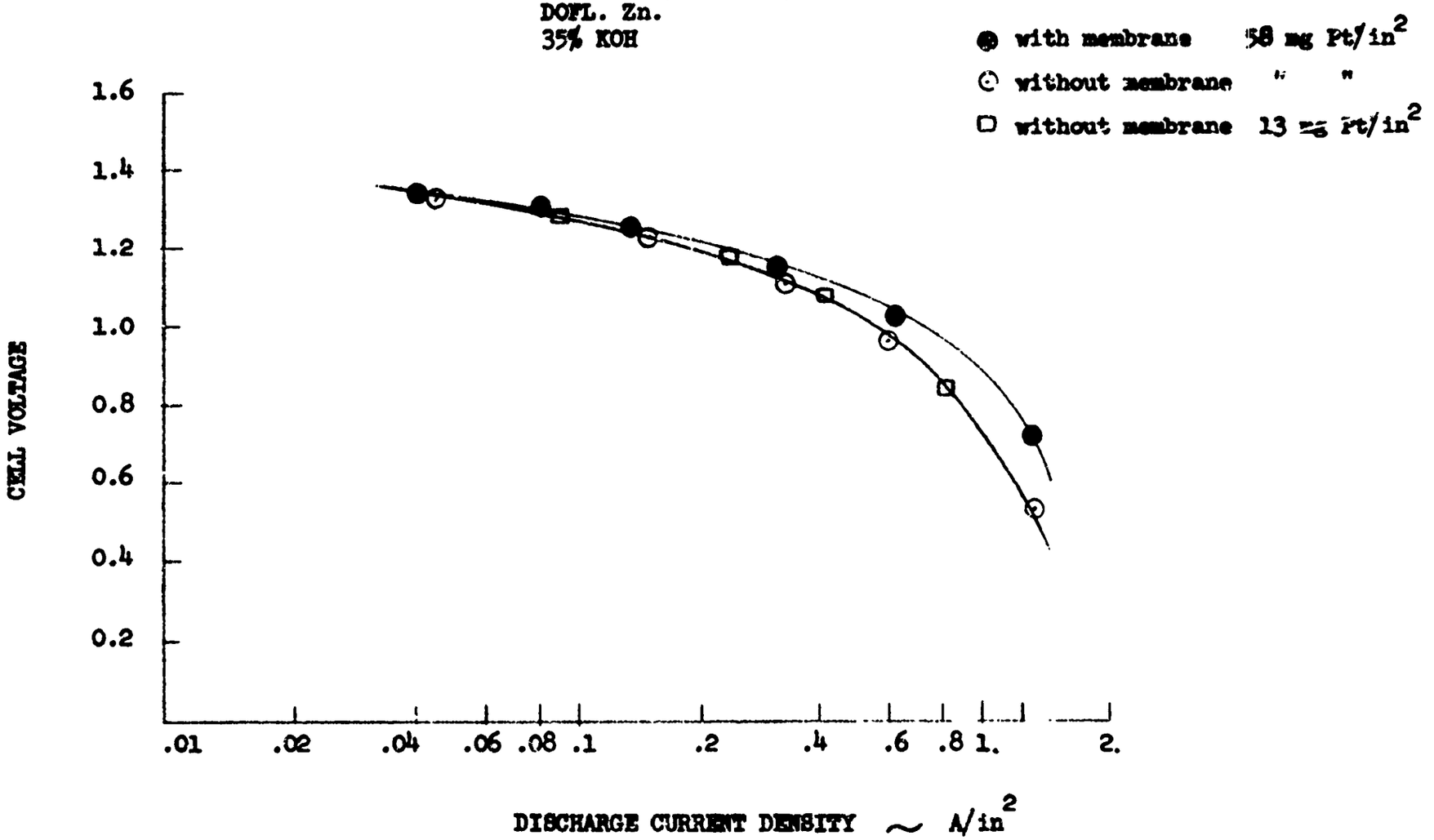


FIGURE 5

CAPACITY DATA

CAPACITY DATA
Zn - Air
Chem. Cell Air Electrodes
Room Temp.
Zn Density = 1.8/cm^3
DOFL Treated Zn

I_d = 200 ma/in^2

● 58 mg Pt/in^2 without membrane
○ 58 mg Pt/in^2 with membrane
■ 13 mg Pt/in^2 with membrane

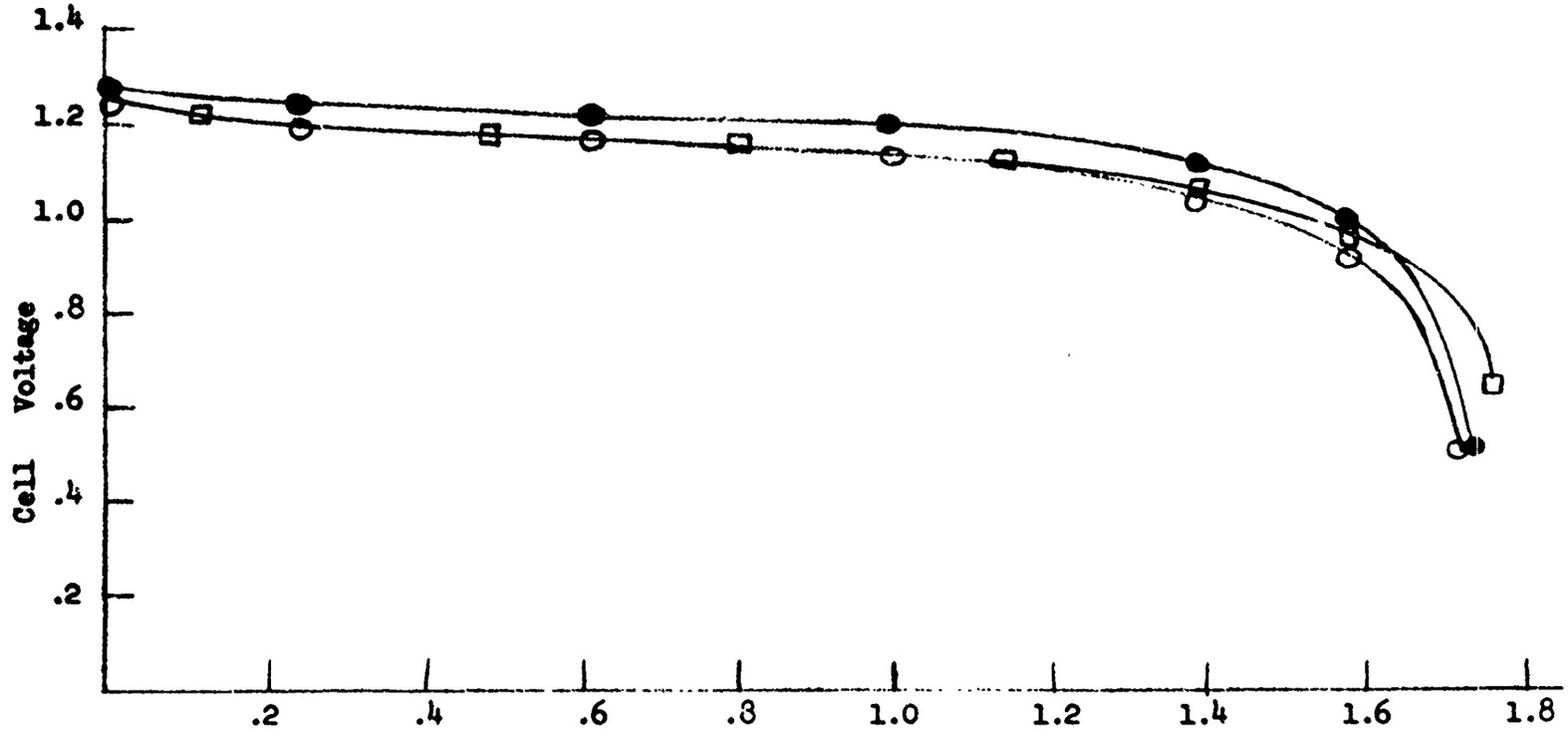


FIGURE 6

Air Electrode Discharge Characteristics
in 3N $Mg(ClO_4)_2$
Mg (AZ 61) Anode
3 N $Mg(ClO_4)_2$ & 1% NaCl
Id. = 130 ma/in^2

Mg (Az 61) Anode
3N $Mg(ClO_4)_2$ & 1% NaCl

□ FSC Air Electrode, (YEC)
△ Chem. Cell Pt Air Electrode
○ Ag/Hg Air Electrode (Amer. Cyan.)

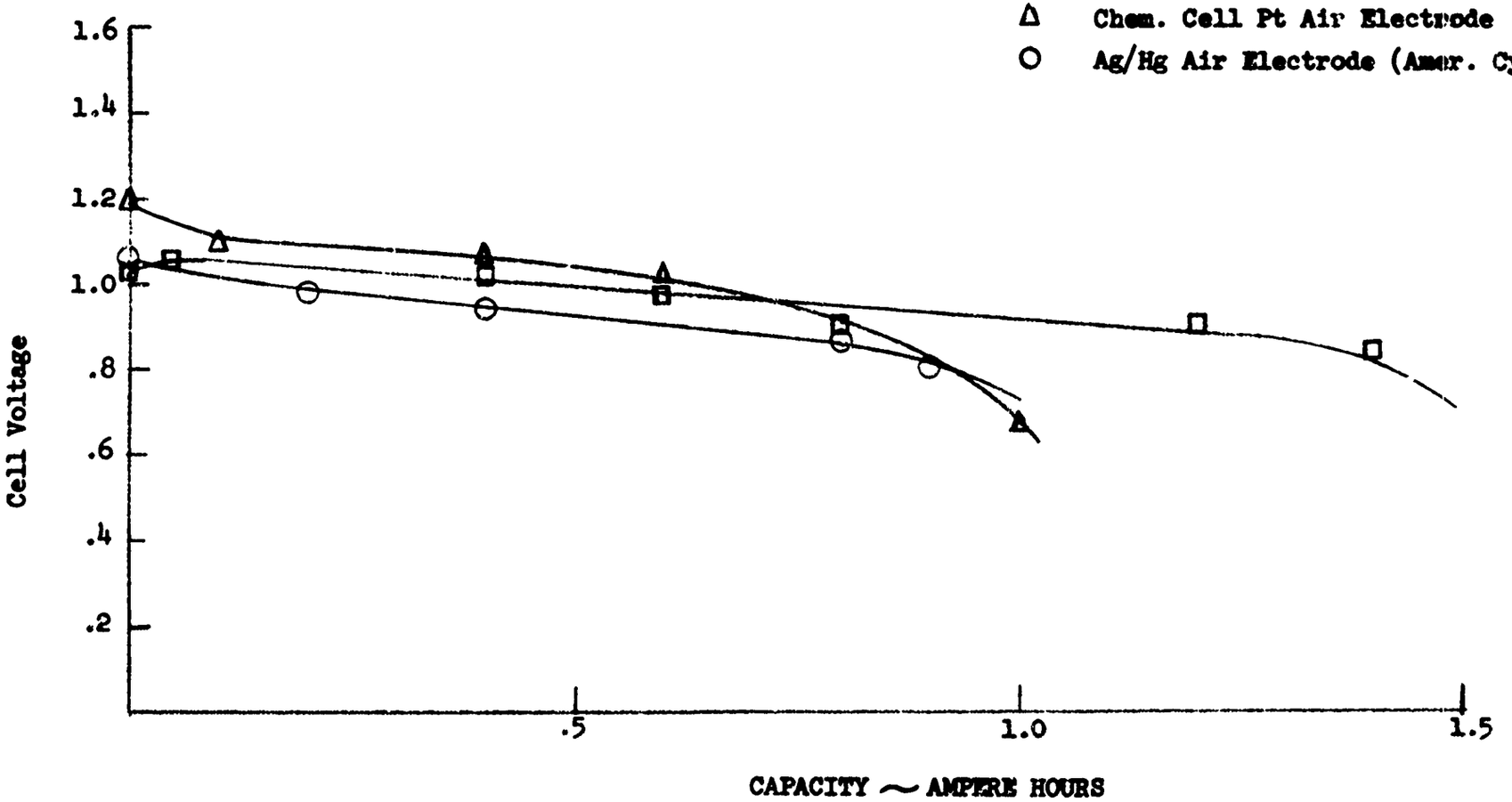


FIGURE 7

FIGURE 7

EFFECT OF ELECTRODE STORAGE ON POLARIZATION CHARACTERISTICS Zn - Air

Room Temp. 35% KOH Zn Density = 2.0 g/cm^3

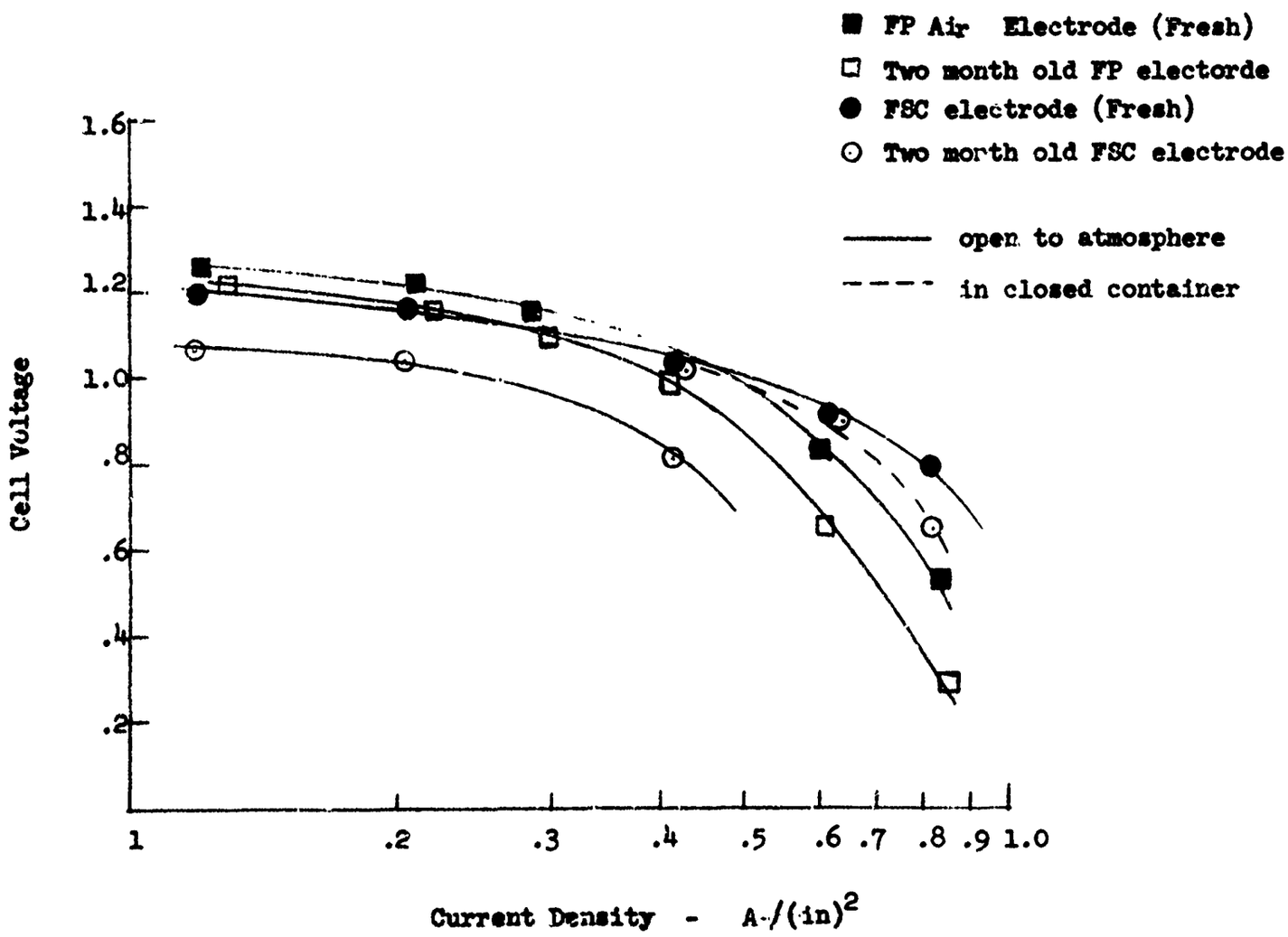


FIGURE 8

POLARIZATION DATA
Zn-Air (FP)
High Temp.
Zn Density = 2.0g/cm^3
Temp = 120°F
31% KOH

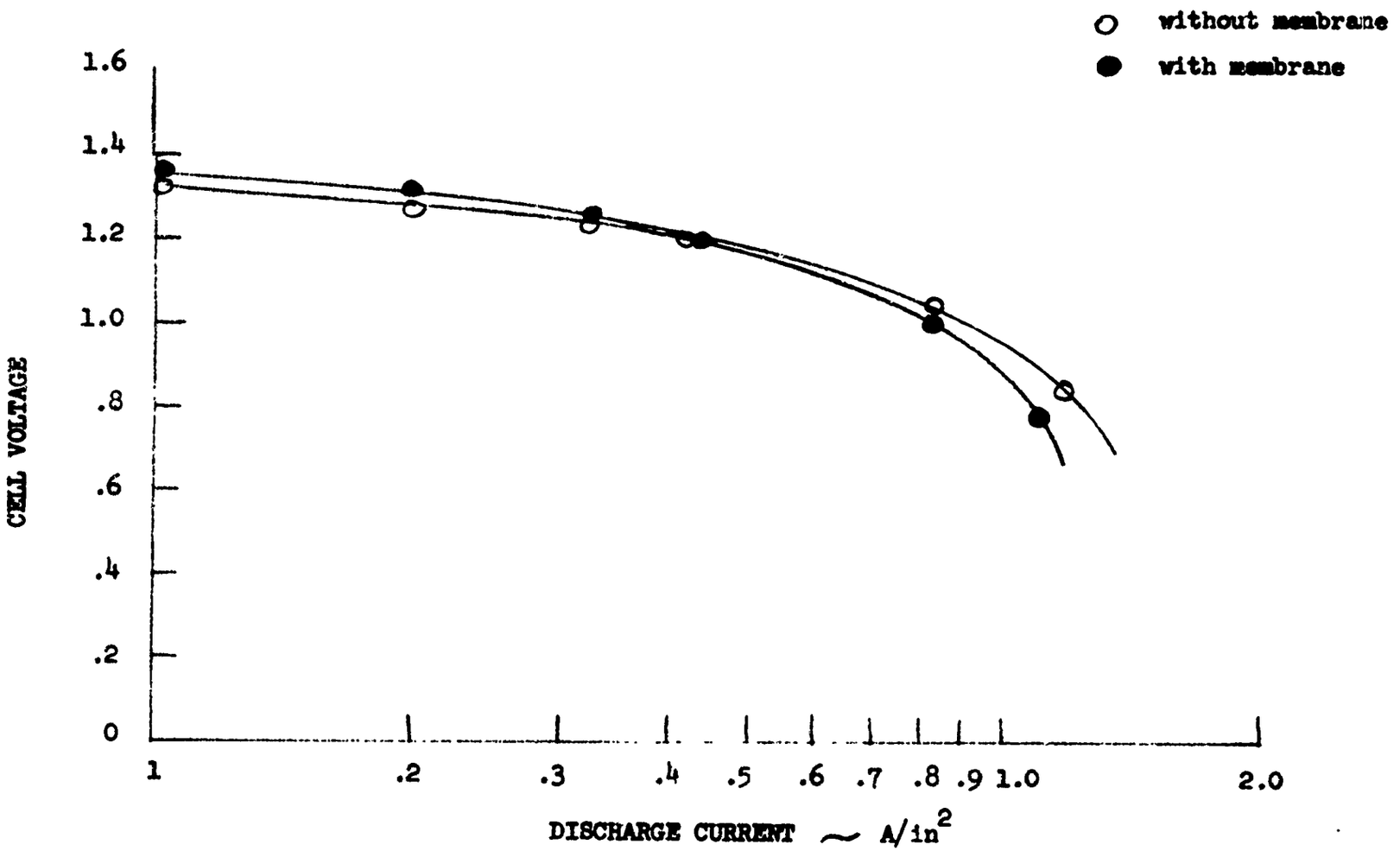


FIGURE 9

HIGH TEMPERATURE PERFORMANCE Zn - Air (FP)

Zn Density = 2.0 g/cm^3
Temp = 120°F
100 mil air spacing
31% KOH

Id = 200 ma/in^2

○ without membrane
● with membrane

Discharged immediately after activation

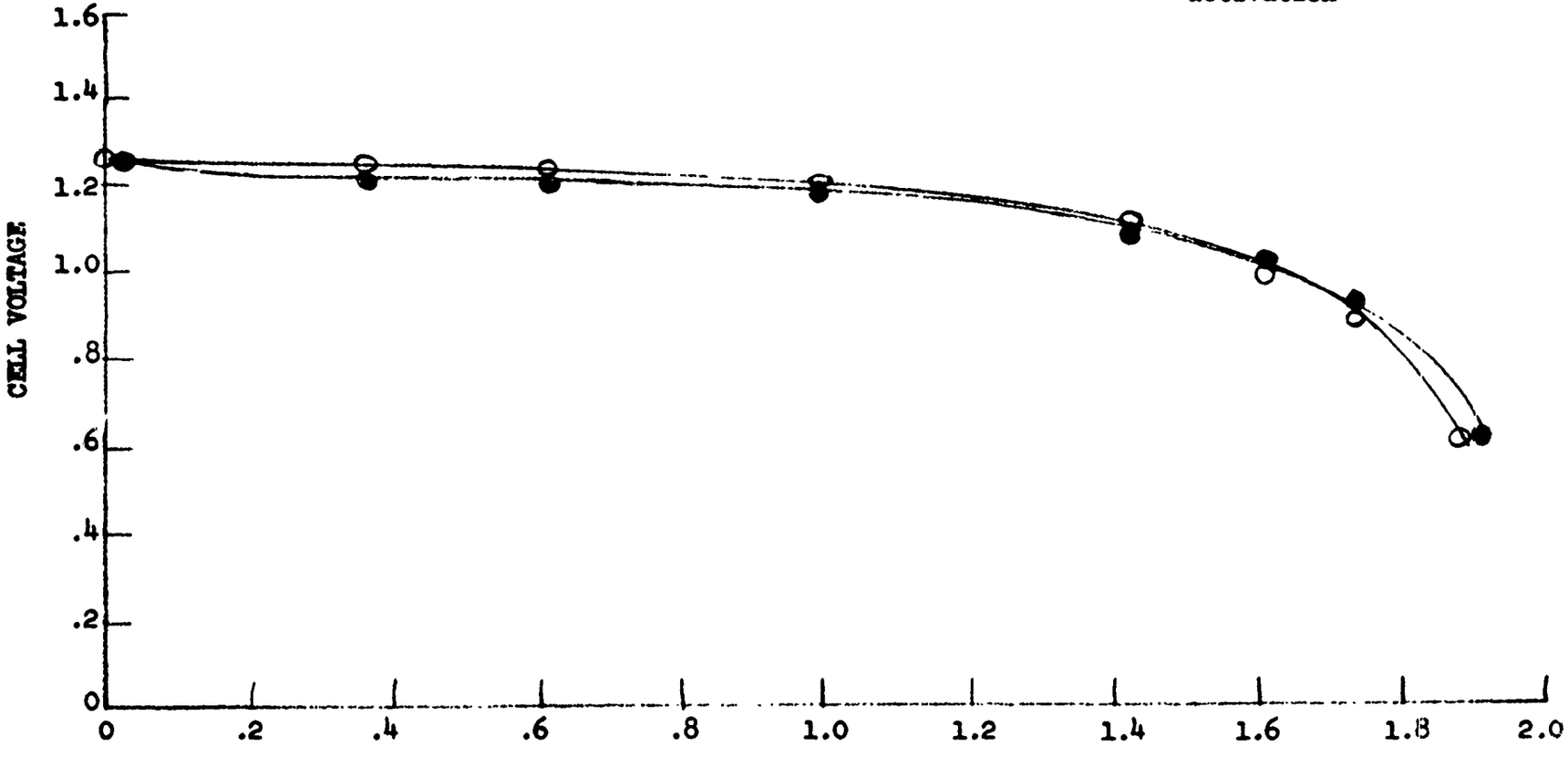


FIGURE 10

EFFECT OF AMALGAMATION ON PERFORMANCE
AT HIGH TEMPERATURE
Zn - Air
Temp = 120°F FP Air Electorde
Id = 16 ma/in^2 ; Anode Area = 2.43 in^2
31% KOH
100 mil air spacing

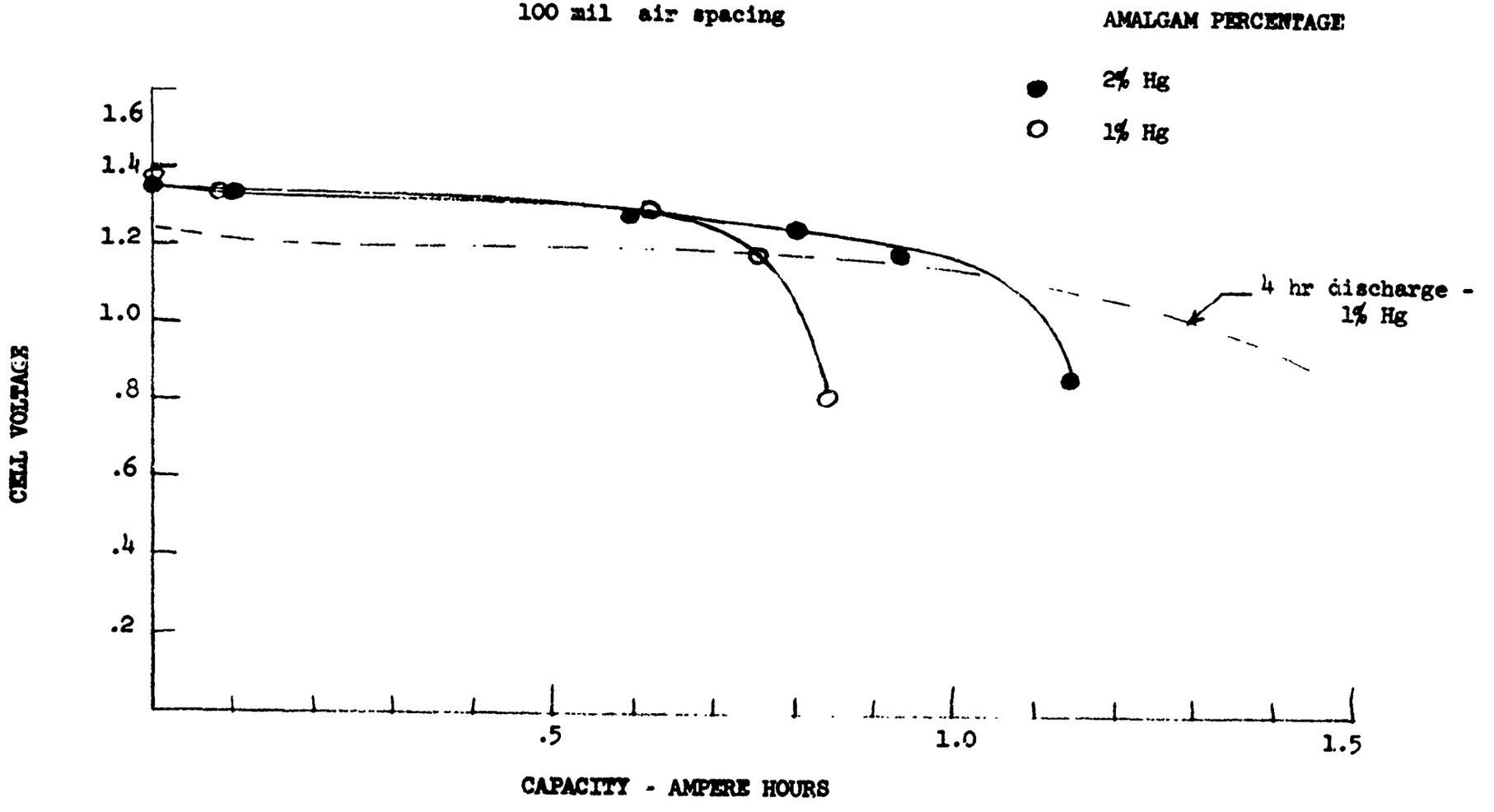


FIGURE 11

HEAT GENERATION AND CAPACITY DATA
AT HIGH TEMPERATURE Zn-Air
FP Air Electrode
Temp = 120°F
Zn Plt. Density = 2.0 g/cm^3
Air Space = 100 mils
Anode Area = 2.43 in^2
2% Hg Amalgam
31% KOH

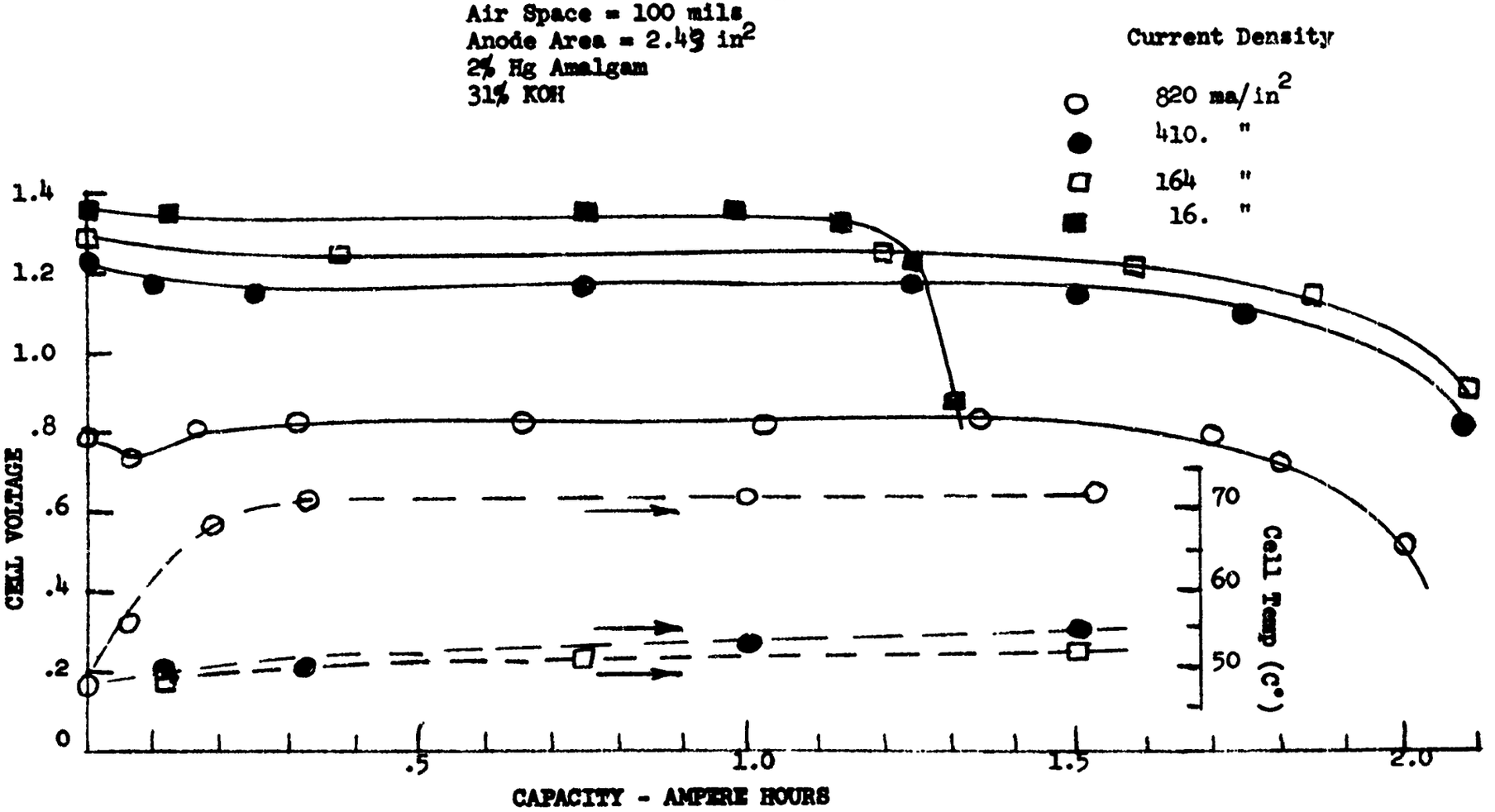


FIGURE 12

EFFECT OF INTERCELL AIR SPACING ON
PERFORMANCE Zn-Air Cells

Temp. = 120°F
Id. = 16 ma/in^2

FP Air Electrode
Zn Plt Density = 2.0 g/cm^3
2% Hg
Anode Area = 2.43 in^2
31% KOH

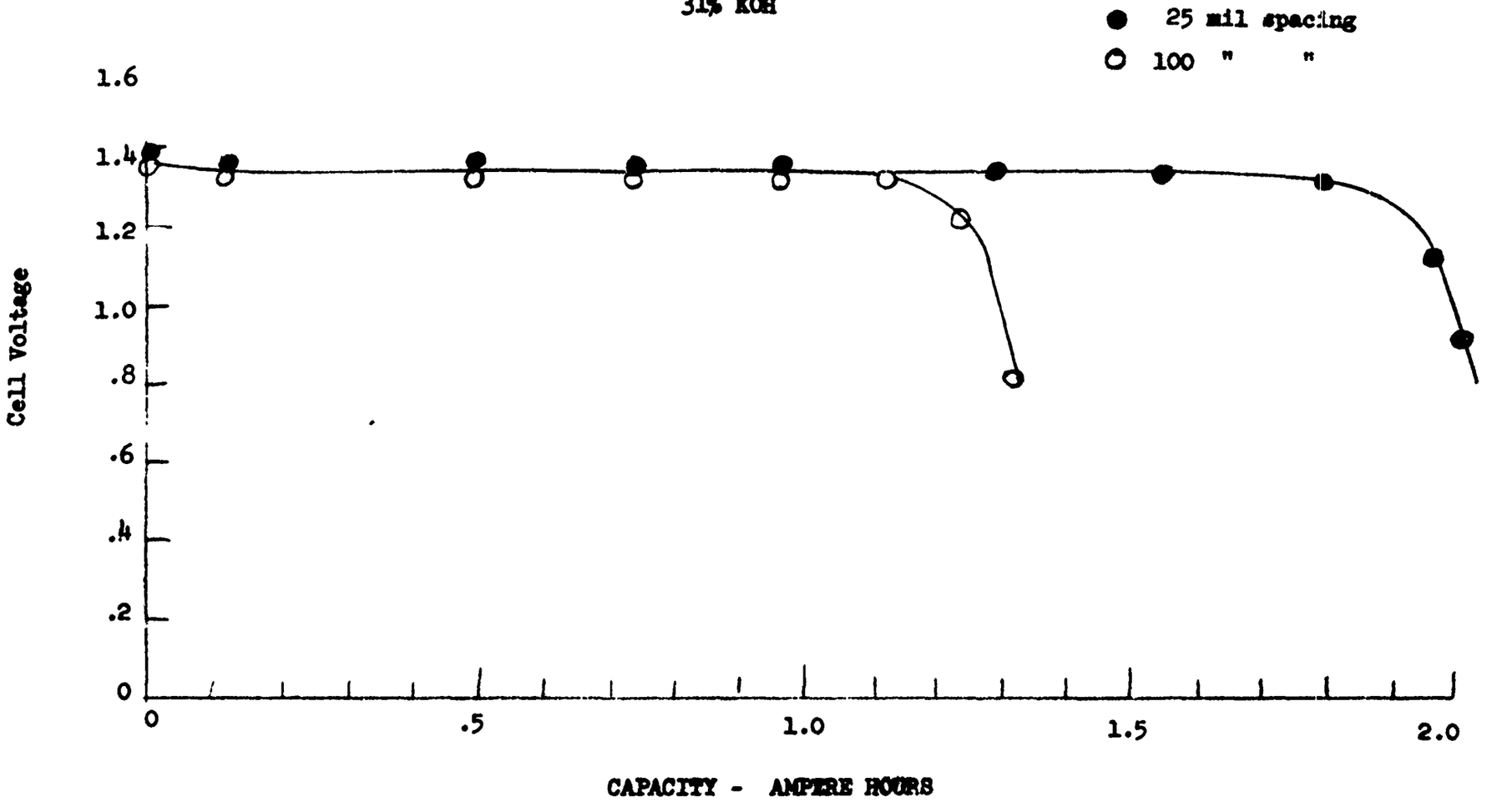


FIGURE 13

EFFECT OF LENGTH OF ACTIVATED STAND
ON POLARIZATION CHARACTERISTICS
Zn-Air (FSC)

Separator - 2 Pellon
1 C-19

31% KOH
Temp = 120°F

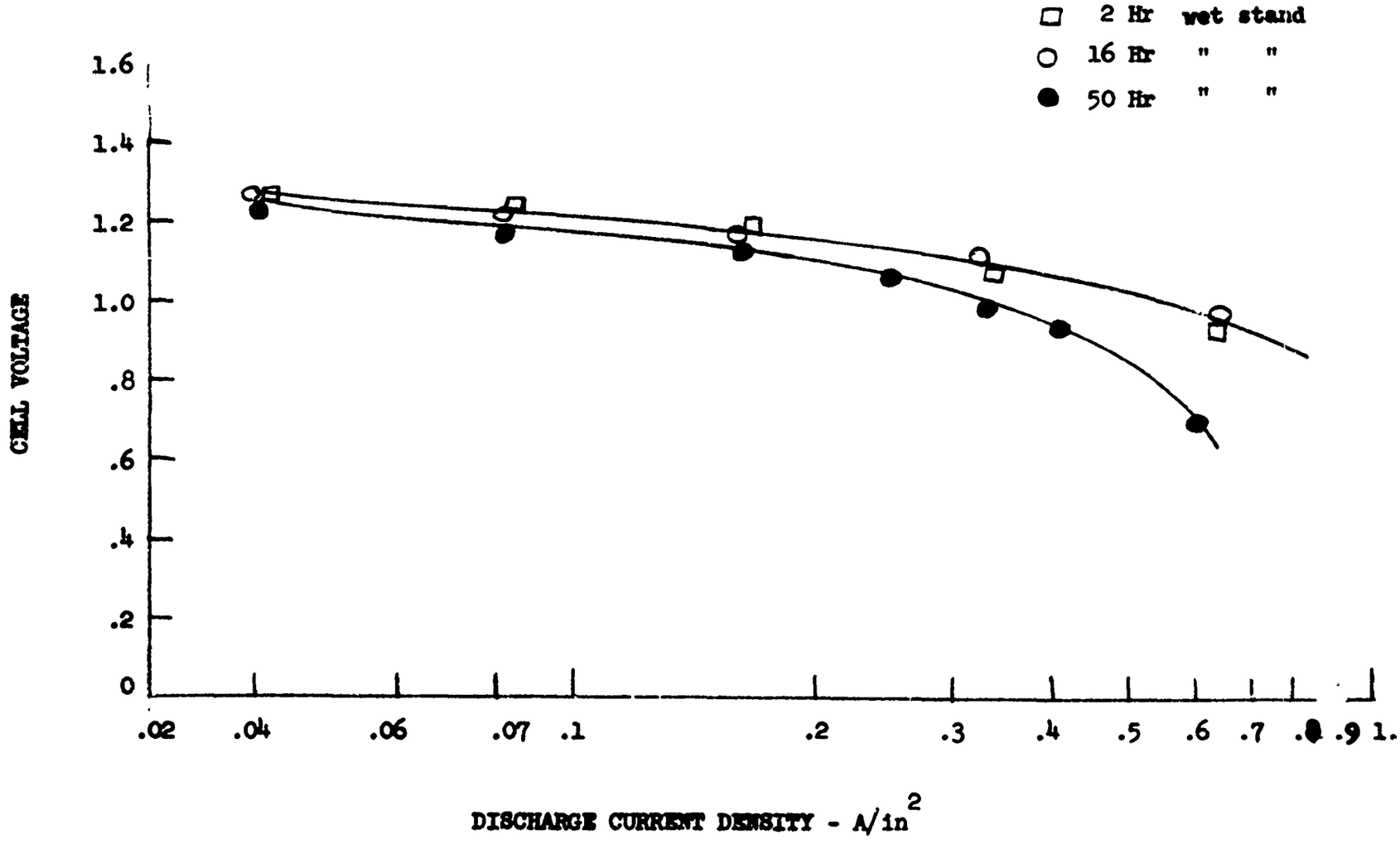
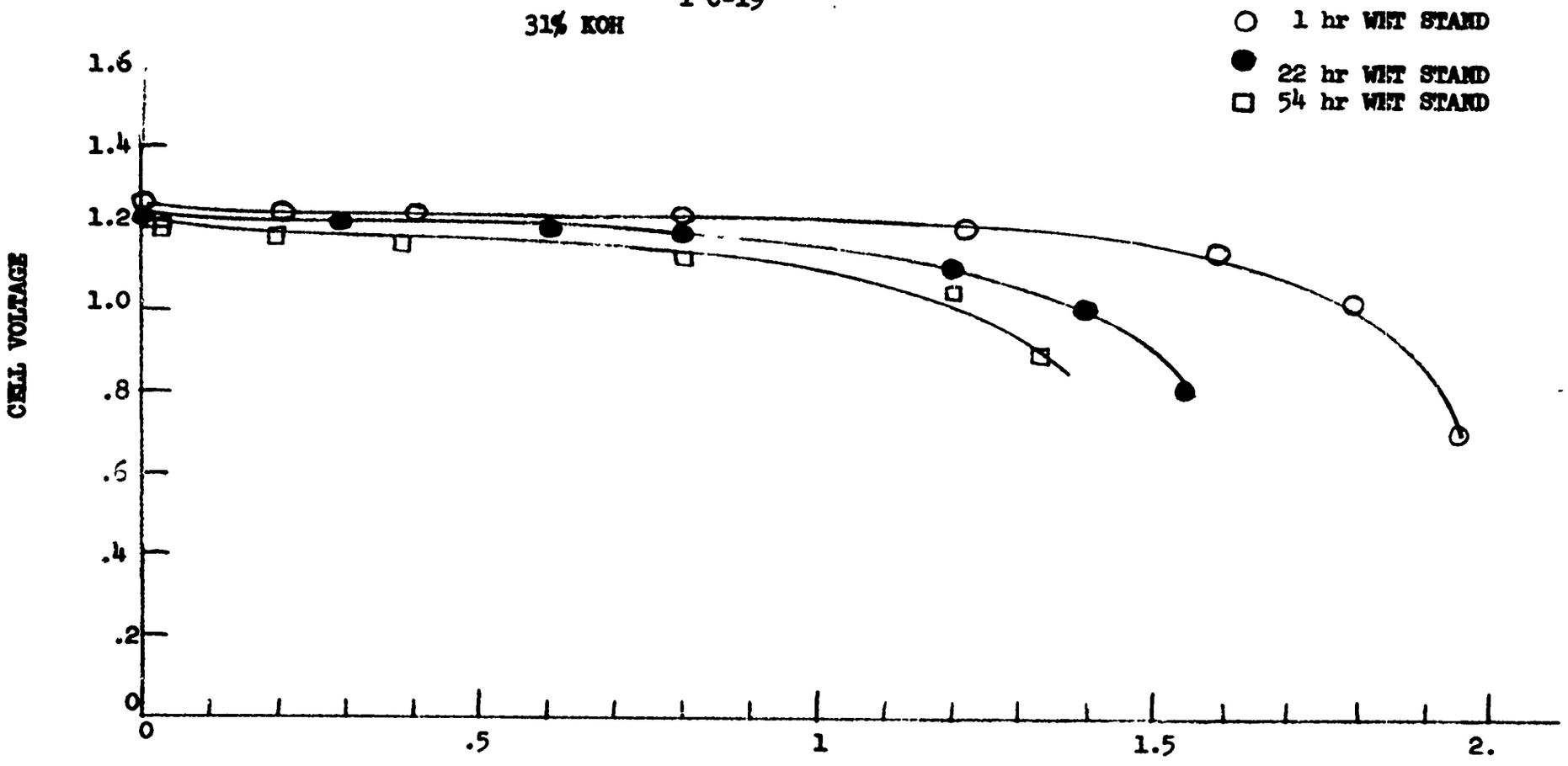


FIGURE 14

EFFECT OF ACTIVATED WET STAND ON
DISCHARGE CAPACITY Zn-Air
(FP)

Temp = 120°F
Zn Density = 2.0 g/cm^3
Zn - 2% Hg
Separator - 2 Pellon
1 C-19
31% KOH

Id = 164 ma/in^2



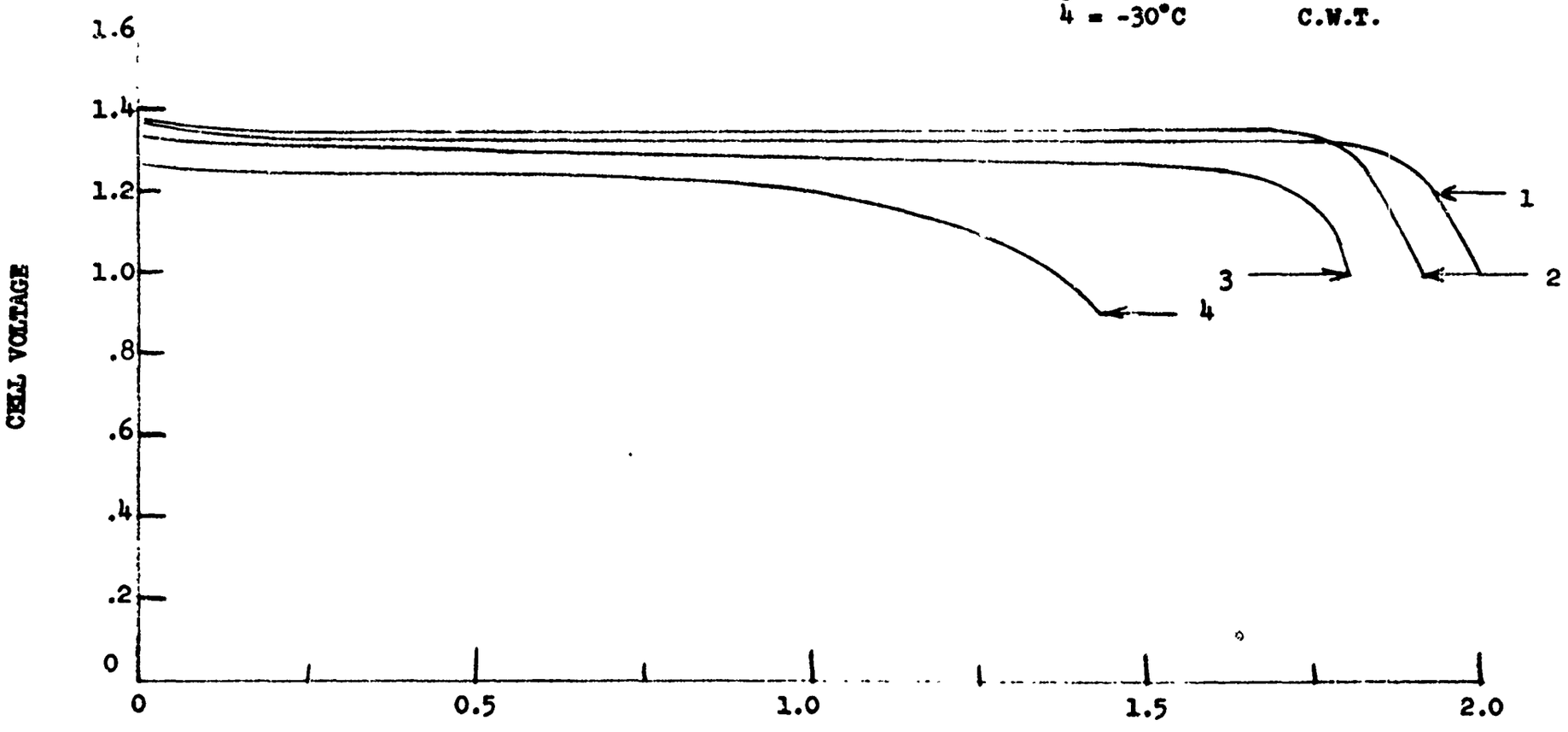
CAPACITY - AMPERE HOURS

FIGURE 15

50 HOUR RATE DISCHARGE CAPACITY DATA
Zn-Air Cells
FP Air Electrode
31% KOH
Zn Wt. = 2.6 g
Plt. Area = 2.49 in^2

Id = 16 ma/in^2

	Temp	Zn Anode Type
1 =	50°C	DOFL + 2% Hg
2 =	25°C	" "
3 =	0°C	" "
4 =	-30°C	C.W.T.



CAPACITY - AMPERE HOURS

FIGURE 16

LOW TEMPERATURE CAPACITY DATA
Zn - Air Cells

Temp = -30°C
Id. = 16 ma/in^2

Zn Density = 1.8 g/cm^3
Anode Area = 2.43 sq. in
31% KOH
FP Air Electrode

Zn Treatment
● C W T
○ DOFL

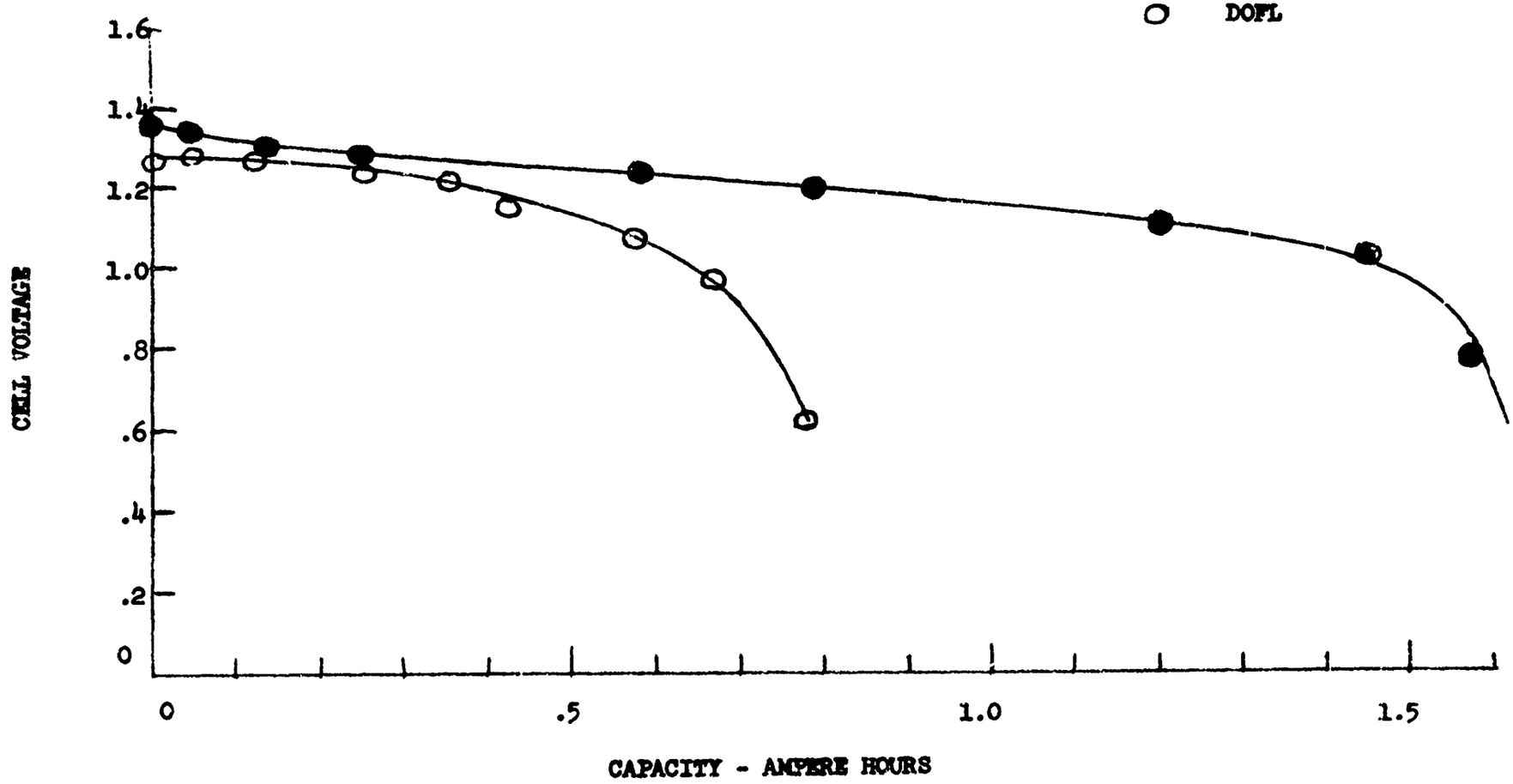


FIGURE 17

25 AMPERE-HOUR Zn-AIR CELL

FIGURE 17

25 AMPERE-HOUR Zn-AIR CELL
CAPACITY DATA
Zn-Air

Room Temp.
Chem. Cell Corp.
Pt Air Electrode
58 mg Pt/in^2

35% KOH
Anode Area = 57 in^2
Zn Plt wt = 36.5 g
Zn density = 1.8g/cm^3

DOFL Treated

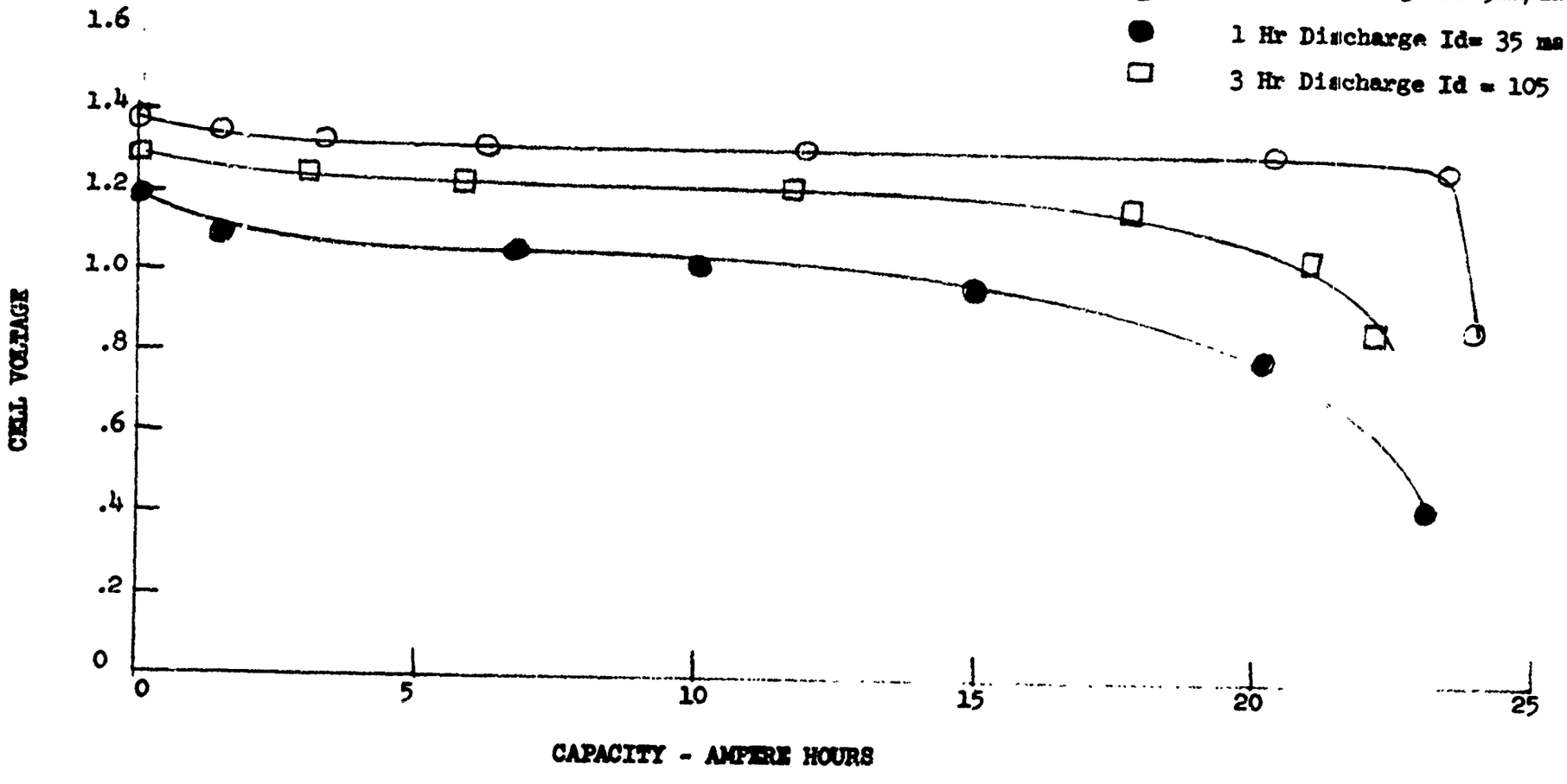


FIGURE 18

25 AMPERE-HOUR CELL PERFORMANCE DATA
Zn - Air

Room Temp

31% KOH
Anode Area = 57 in^2
Zn Plt. wt. = 37 g

FP Air Electrode

Discharge Rate
○ Id = 9 ma/in^2
□ Id = 105 ma/in^2
● Id = 351 ma/in^2

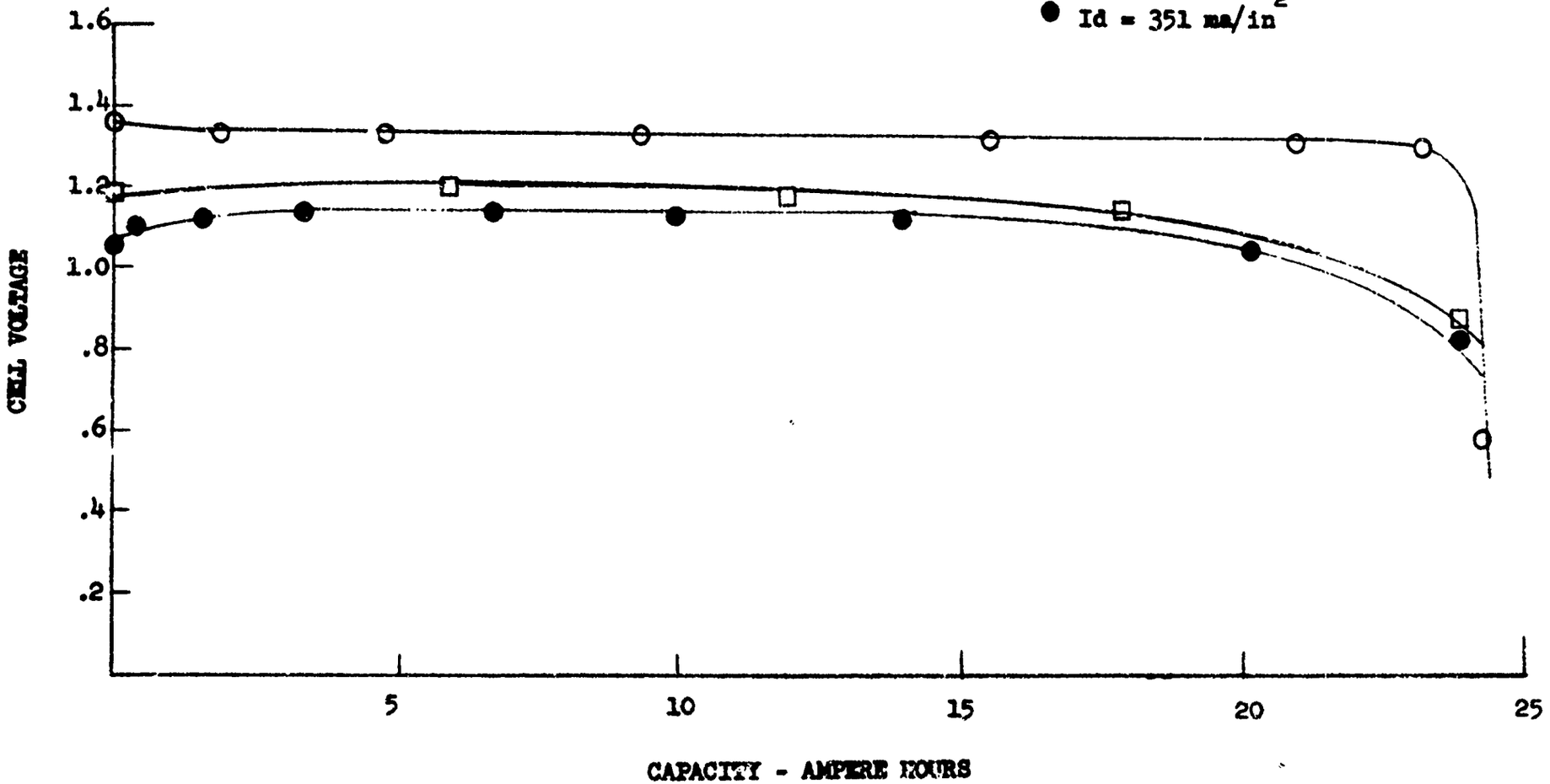


FIGURE 19

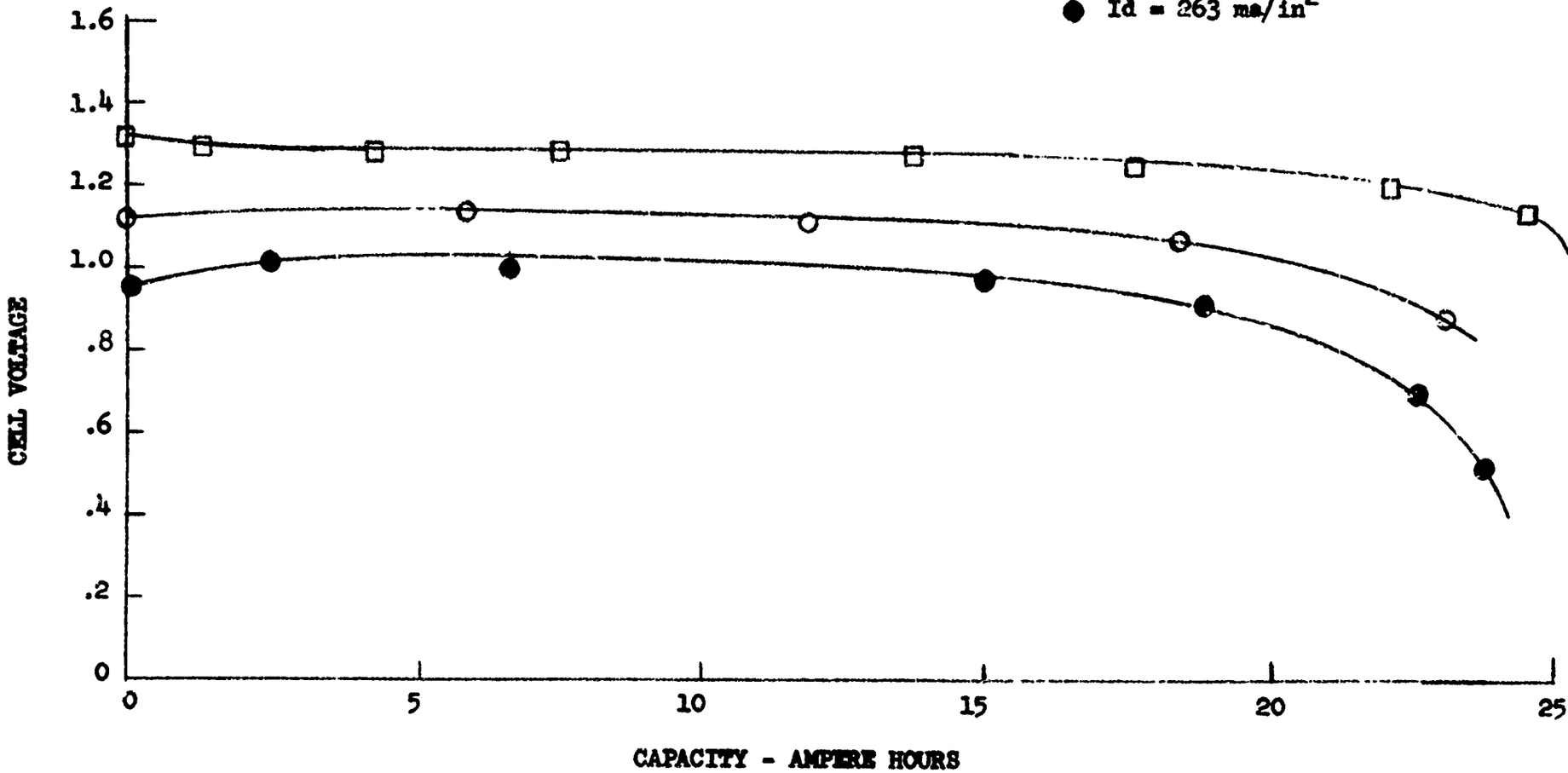
25 AMPERE-HOUR CELL PERFORMANCE DATA
Zn - Air

Room Temp

31% KOH
Anode Area = 57 in^2
Zn Plt. Wt. = 37 g

FSC Air Electrode

Discharge Rate
□ Id = 9 ma/in^2
○ Id = 105 ma/in^2
● Id = 263 ma/in^2



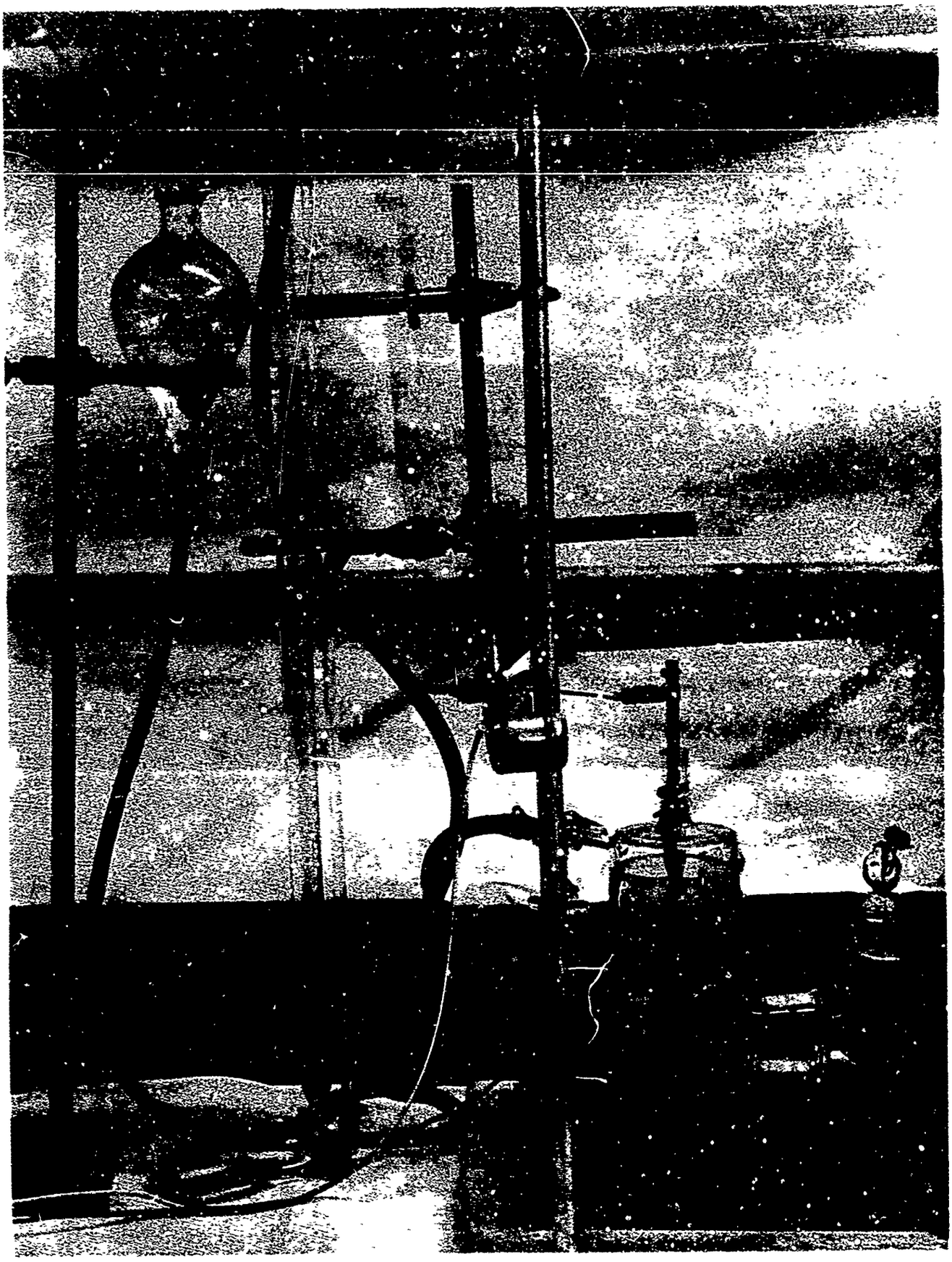


FIGURE 20

POLARIZATION APPARATUS

FIGURE 21

CORROSION RATE AS A FUNCTION OF CURRENT DENSITY

Mg (AZ - 61) Anode

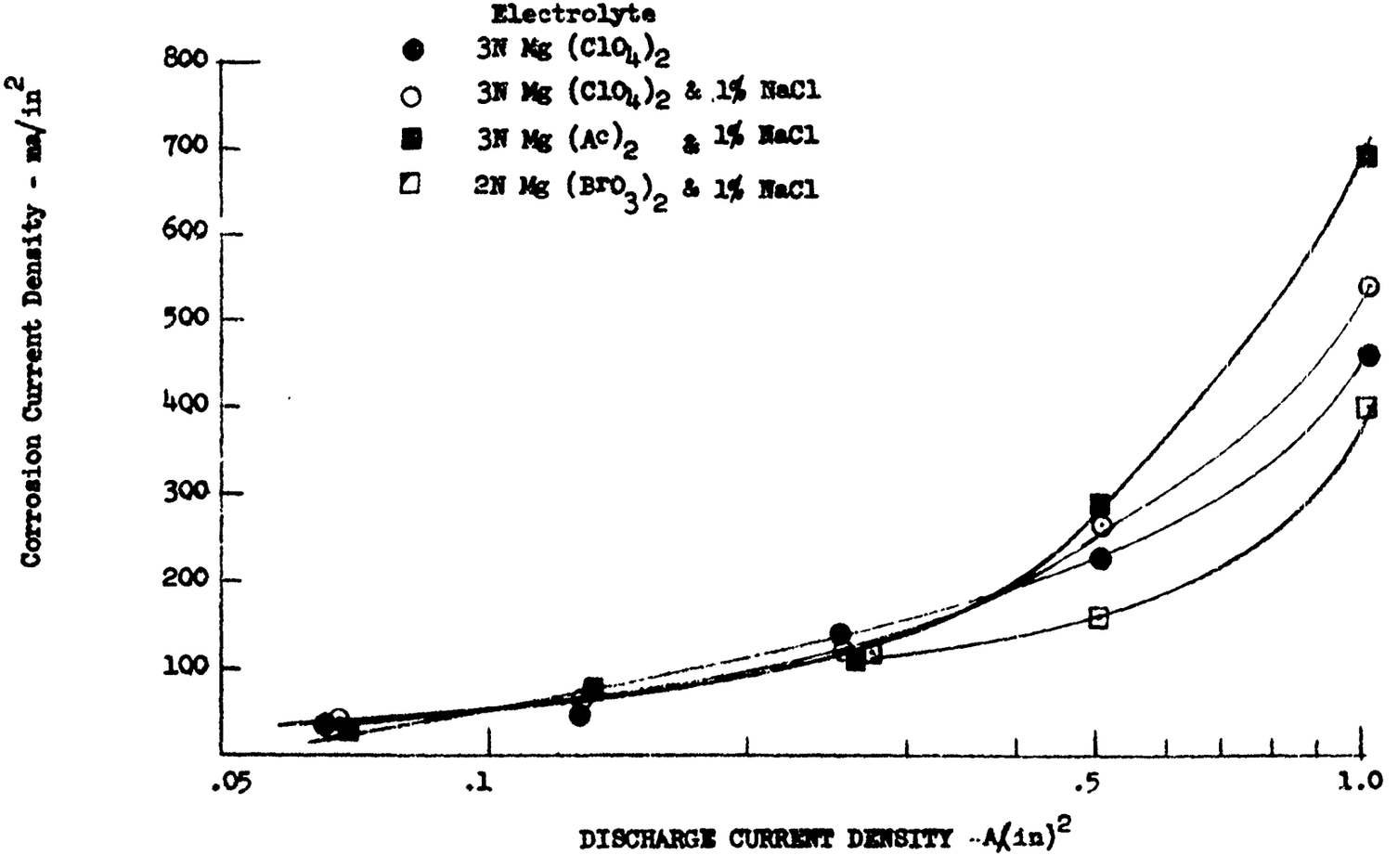


FIGURE 22

POLARIZATION DATA FOR Mg IN FREE ELECTROLYTE

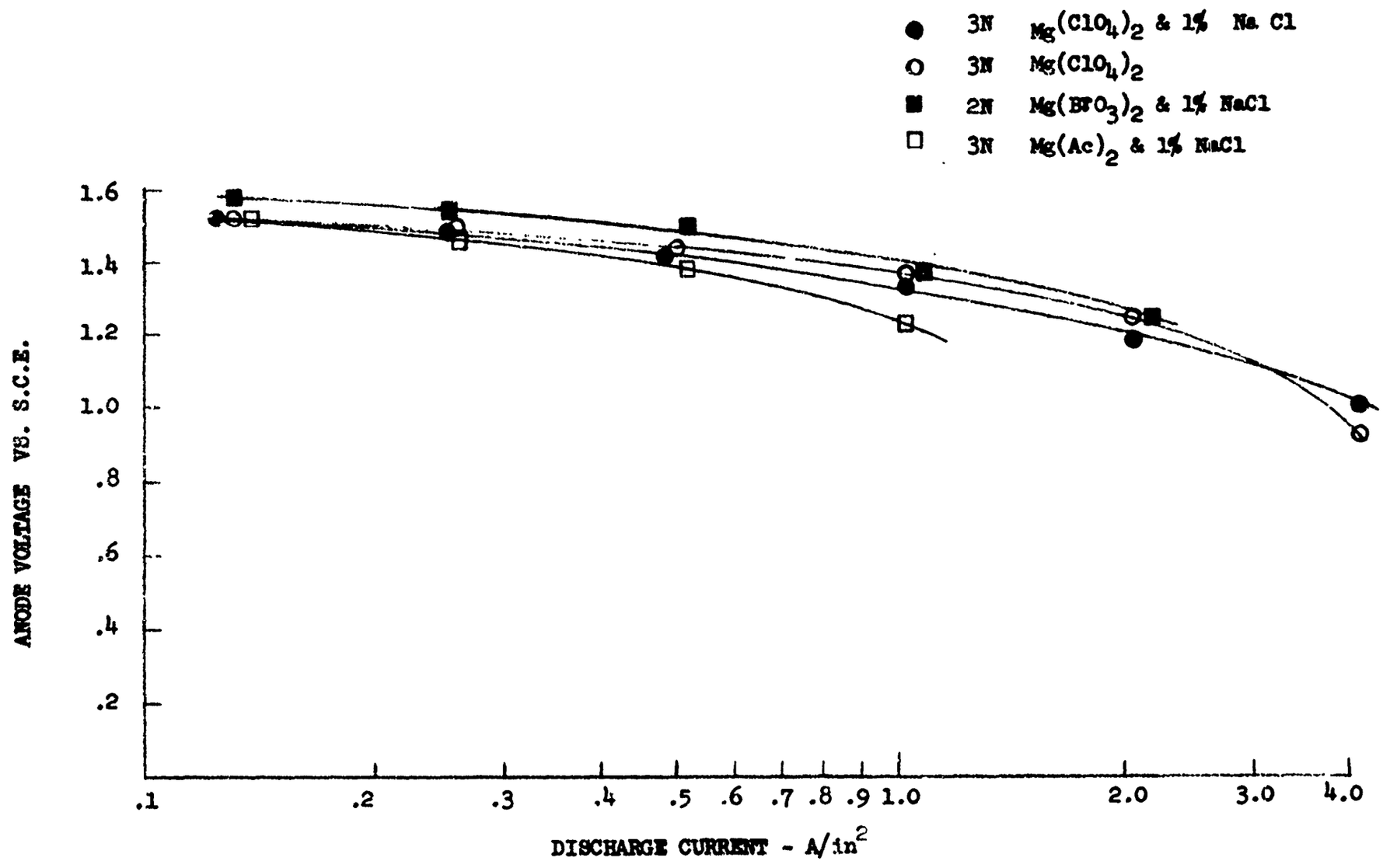


FIGURE 23

CAPACITY DATA – Mg ANODE
3N $MgClO_4$ & 1% NaCl

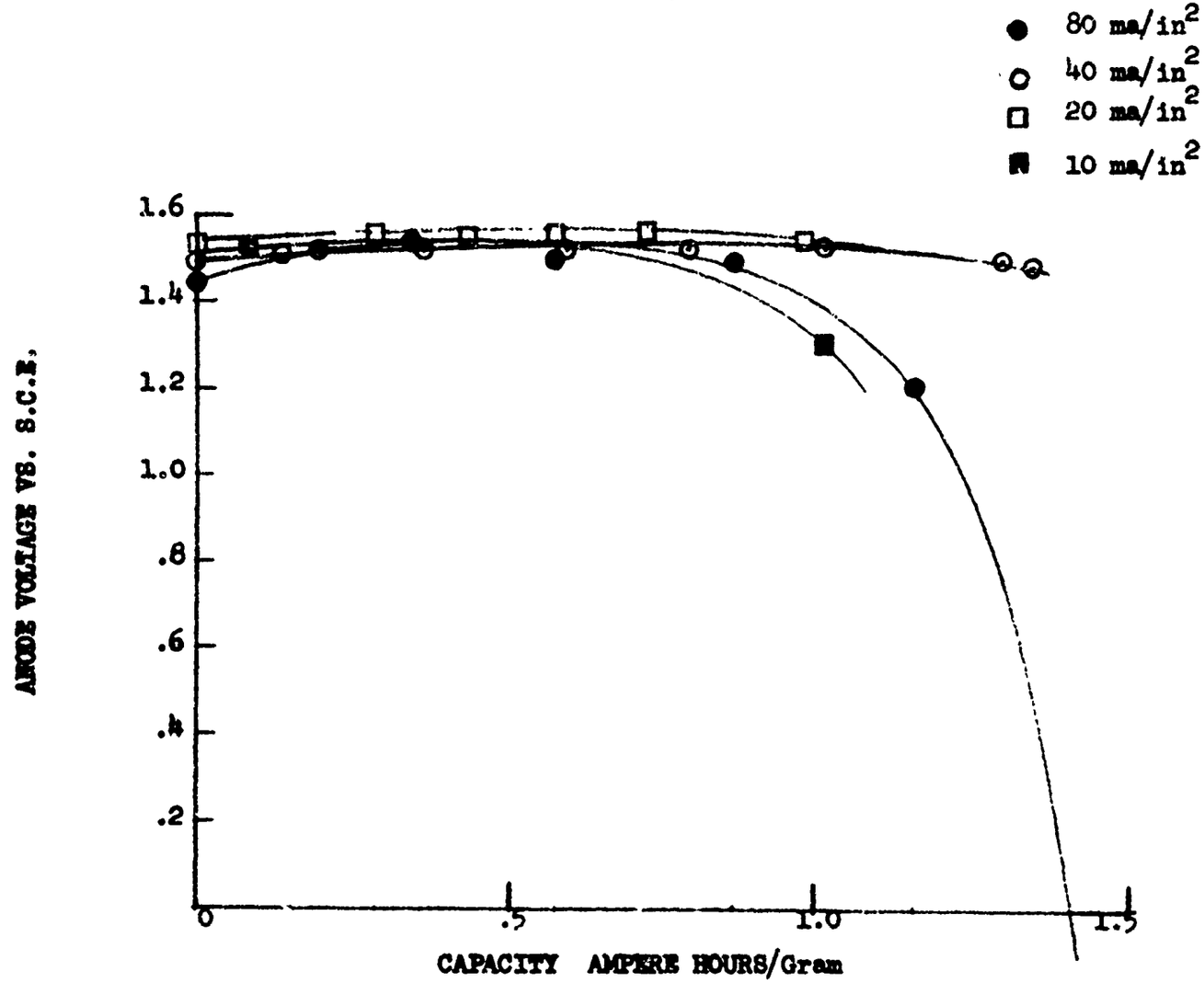


FIGURE 24

POLARIZATION DATA
Mg - Air

FSC Air Electrode

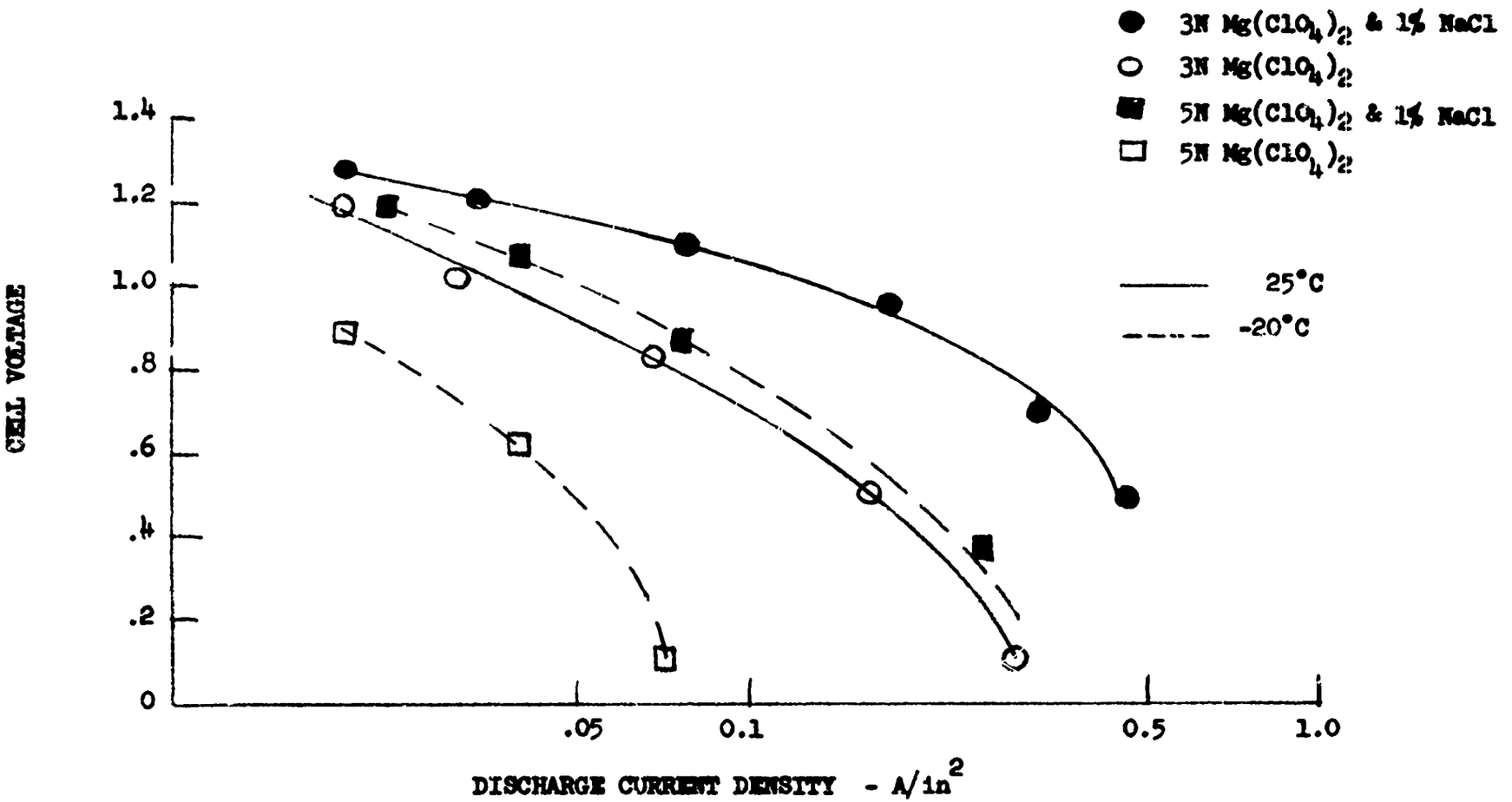


FIGURE 25

POLARIZATION DATA Mg-Air(FP)
AZ-61 Mg Alloy
Room Temp.

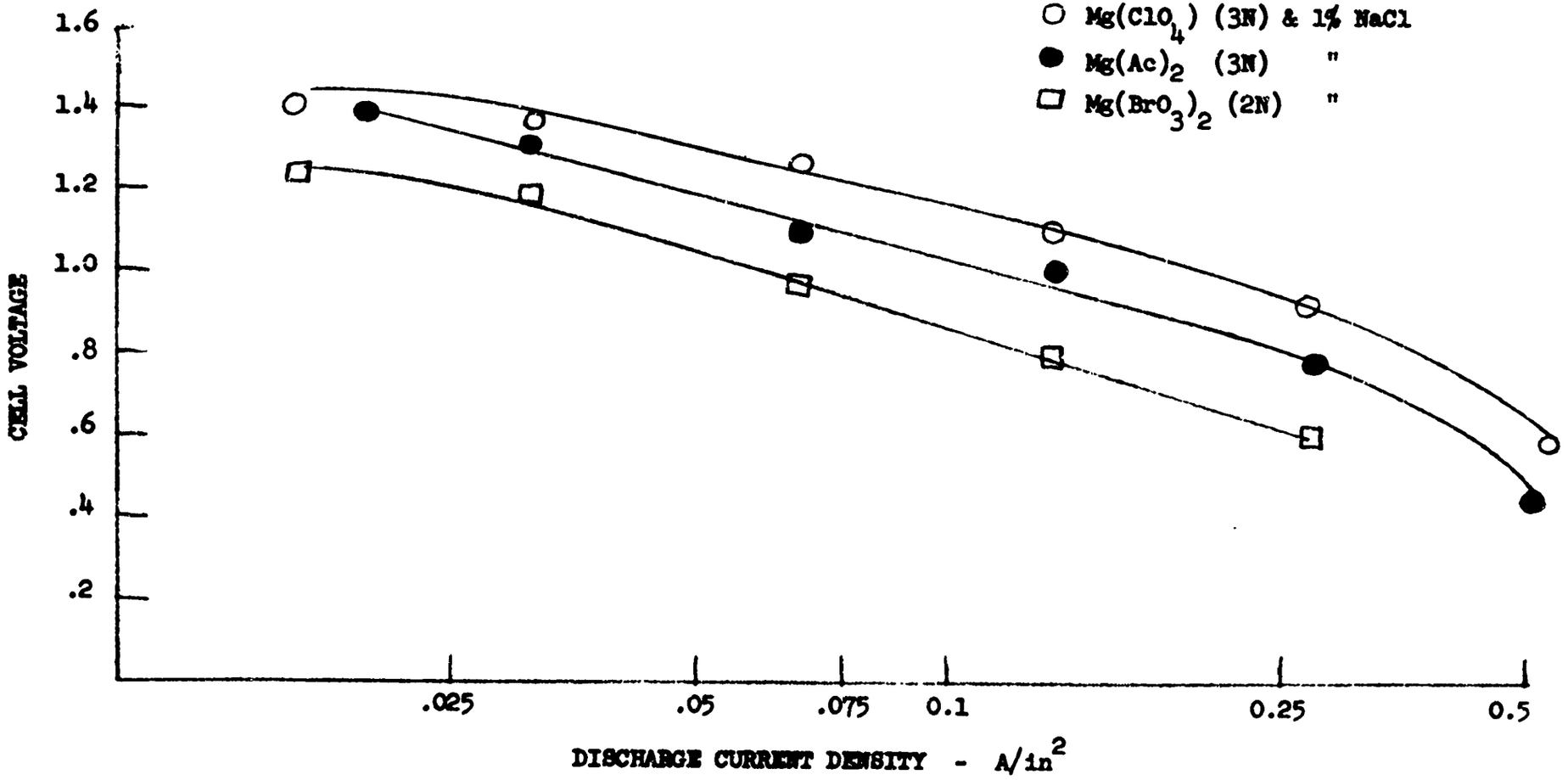
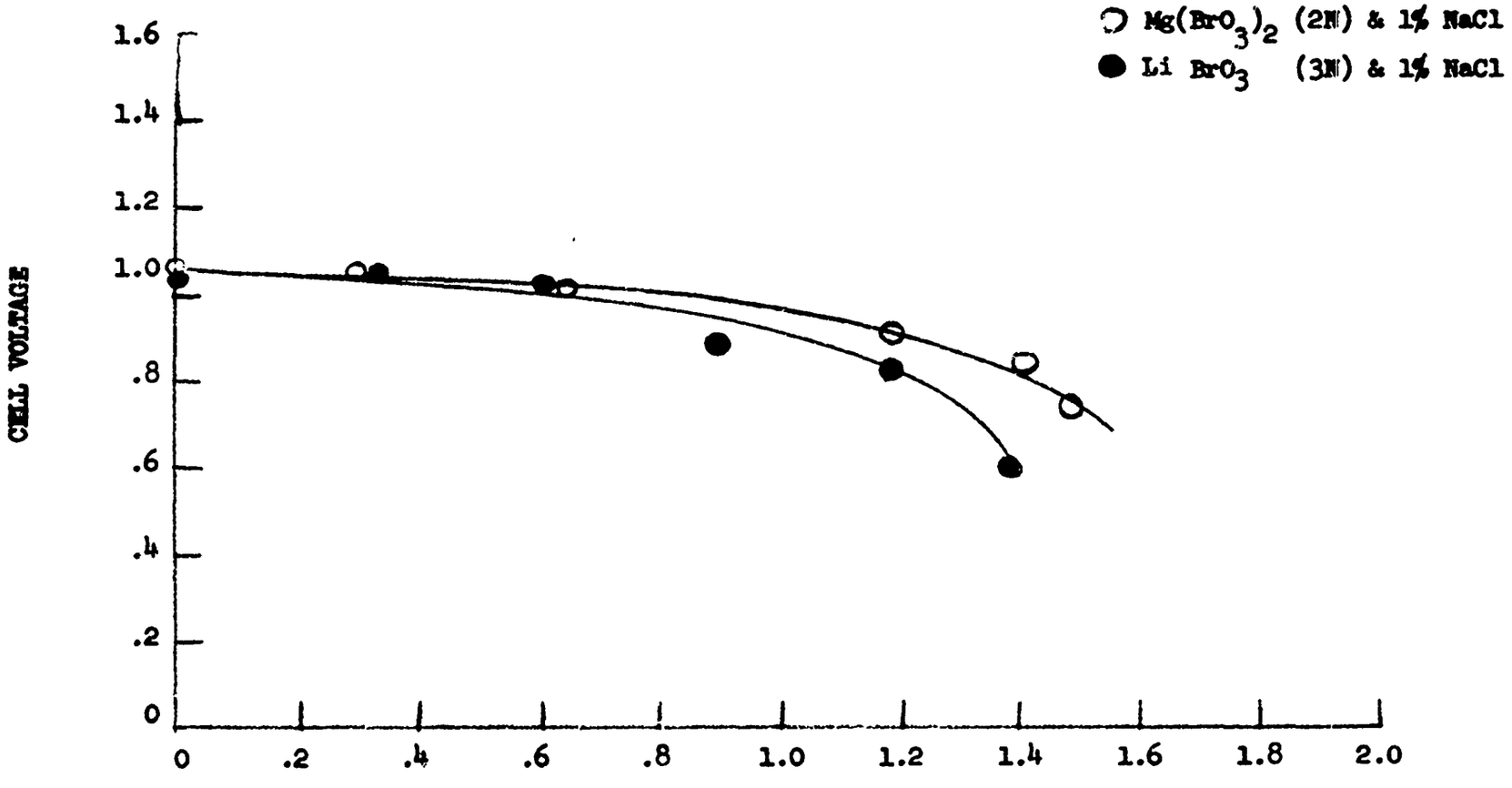


FIGURE 26

Mg - AIR DISCHARGE PERFORMANCE
AE-61 Mg Alloy
FP Air Electrode
Room Temp.
Id = 150 ma/in^2
Wt.Mg = 1.3g



CAPACITY - AMPERE HOURS

CAPACITY - AMPERE HOURS

FIGURE 27

Mg - Air CELL DISCHARGE PERFORMANCE

AZ-61 Mg Alloy

Room Temp Mg wt. = 1.3g
FSC Air Electrode
$Mg(ClO_4)_2$ - 3N
1% NaCl

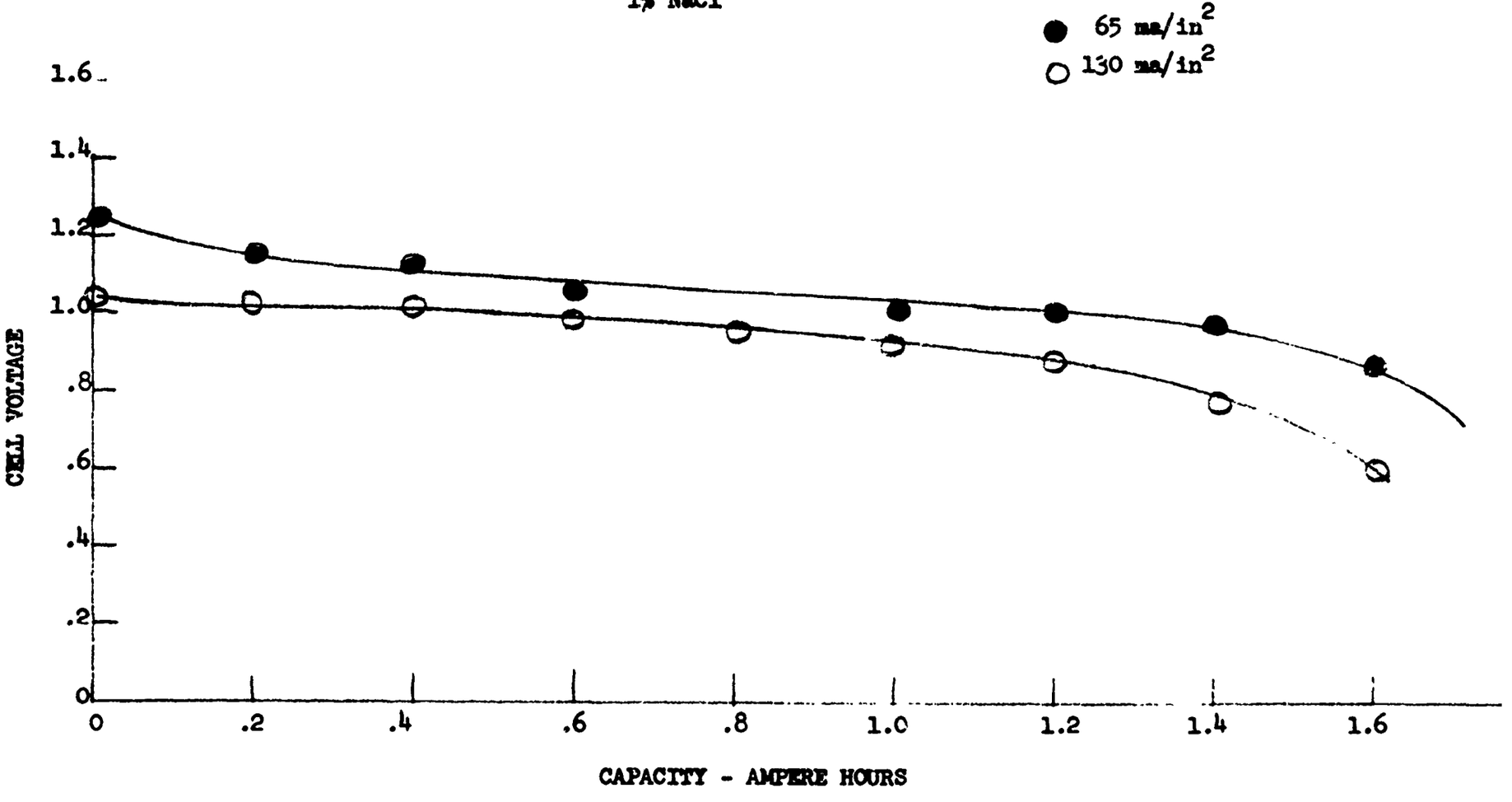


FIGURE 28

POLARIZATION DATA
Al - Air

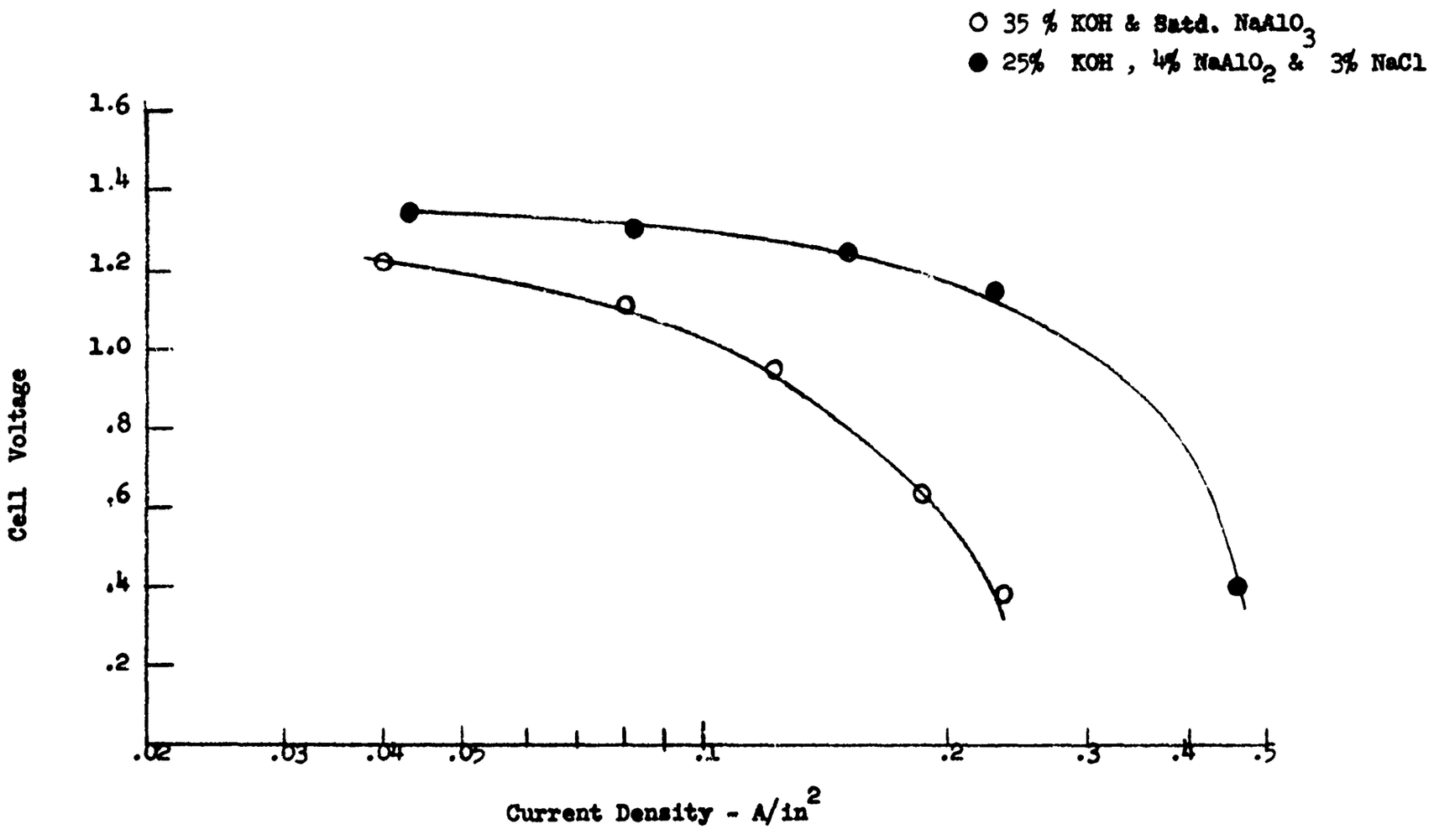


FIGURE 29

HEAT TRANSMISSION OF METAL — AIR CELLS

Air Spacing = .100"

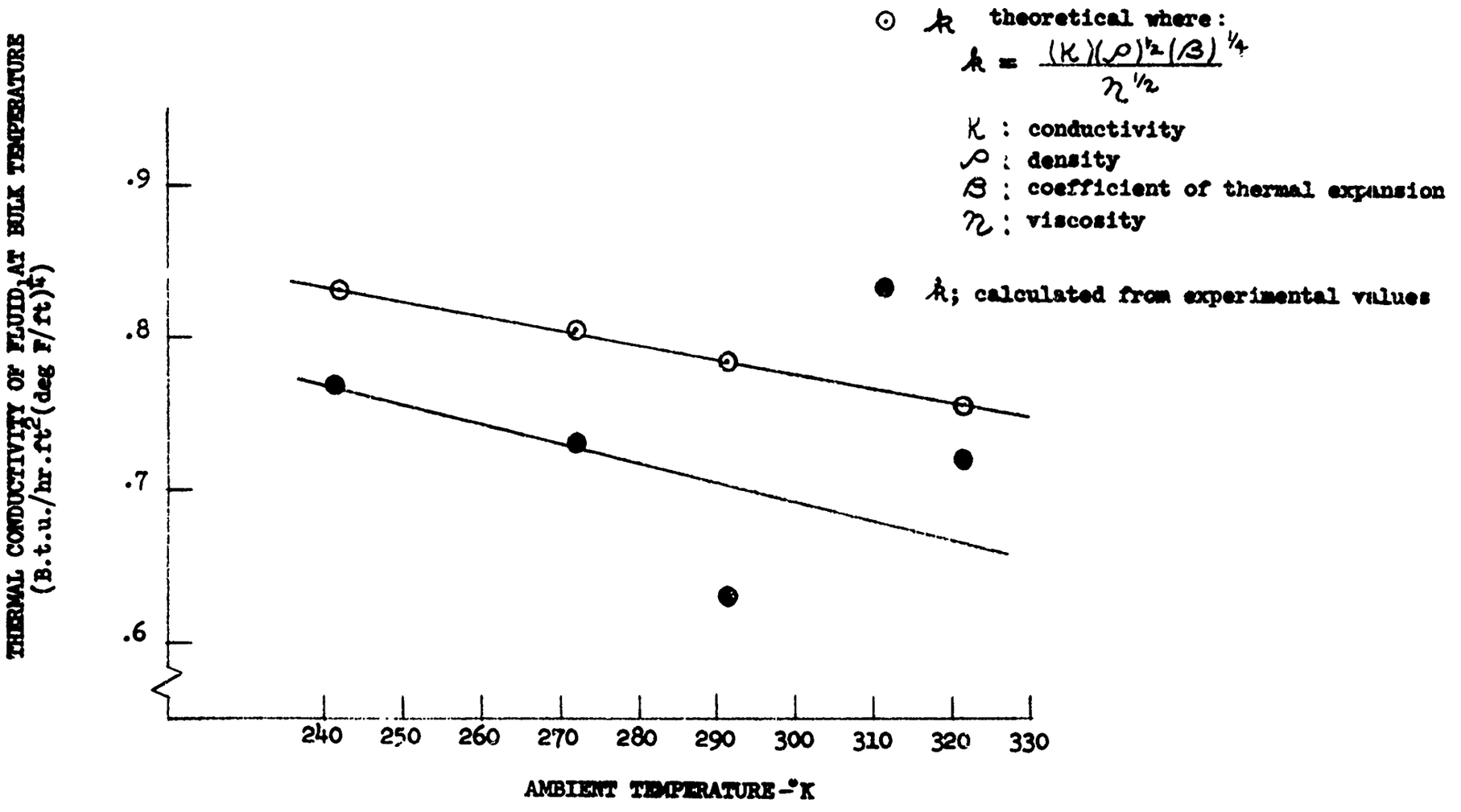


FIGURE 30

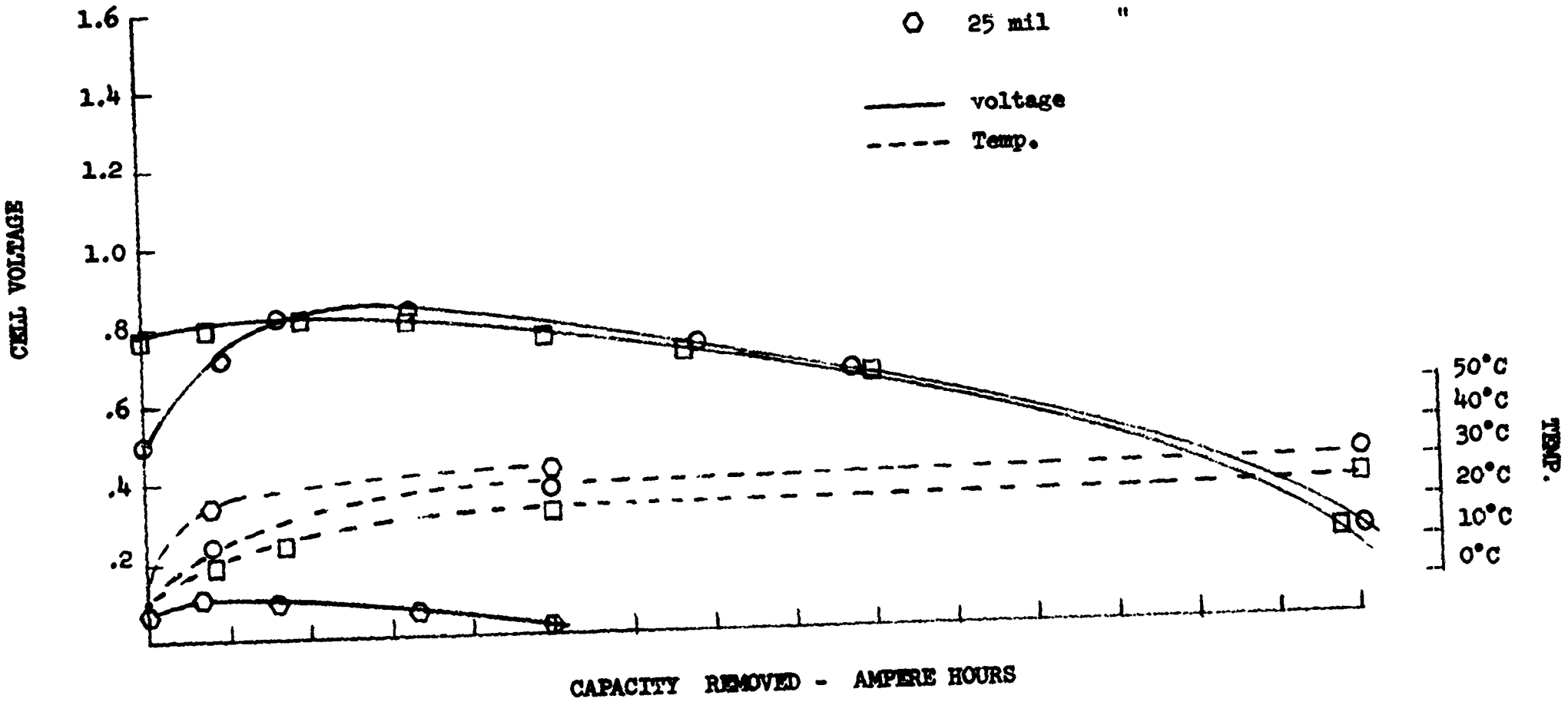
HEAT TRANSFER - CAPACITY DATA AS A FUNCTION OF INTERCELL AIR SPACING

31% KOH
Low Density Zn (1.8 g/cm^3)
DOFL Treated Zn
Temp = 0°C

Id = 820 ma/in^2

□ 100 mil air spacing
○ 50 mil "
○ 25 mil "

——— voltage
- - - - Temp.



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4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Quarterly - 1 October 1965 - 31 December 1965

5 AUTHOR(S) *(Last name, first name, initial)*

Charkey, Allen

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13. ABSTRACT

This report covers the work done during the second quarter of the investigation for the U.S. Army Electronics Command. The study is being conducted to determine the performance characteristics and operational parameters for various metal-air couples. The anode materials being examined are Al, Ba, Ca, Mg, and Zn. They must discharge efficiently at any temperature from -25°F to 125°F at rates from the 30 minute to 50 hour.

The most favorable system in watt-hour per pound performance appears to be the zinc-air cell. During this quarter favorable high temperature discharge performance was obtained by keeping air spacing to a minimum.

Some of the problem areas encountered have been loss of water and excessive carbonation of the electrolyte at 120°F. This results in poor performance and decrease in shelf life.

Several methods for increasing activated shelf life at room temperature have been studied. The most promising appears to be the use of a "parasitic" drain across the cell terminals to delay flooding. At present, shelf life up to one month has been achieved with minimal capacity loss.

The investigation of the magnesium anode during this quarter has included a study of several electrolytes to determine compatibility with both electrodes. In all cases, best performance was obtained in a "free" electrolyte system.

The magnesium-air test cells, used only for exploratory studies, delivered specific energies of 50-55 Watt-hrs./lb. This could be improved substantially

(Continued on Attached Sheet)

DD FORM 1 JAN 64 1473

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by increasing the thickness of the anode and decreasing the quantity of free electrolyte.

The investigation of calcium, aluminum, and barium air systems is still in an early exploratory stage. Particular interest however, is being given to calcium in an organic-aqueous electrolyte with various corrosion inhibiting agents. It appears that the air electrode will also function in this modified aqueous system.

Preliminary data for pure aluminum anodes is only moderately favorable in KOH electrolytes containing ZnO. The use of alloys to decrease corrosion appears warranted.

Heat transfer by means of air convection has been studied over the entire temperature range (-25 to +125°F) for the 2C through the C/50 rate of discharge. The testing units employed the zinc-air couple, but the heat transfer and air convection data are suitable for any metal-air battery design. This experimental investigation also indicated that low temperature bootstrap heating operation will be feasible for a zinc-air battery. (Author)

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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